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Inhibition of Photochemical Processes by a Hydroxyl Group in the Photochemistry of a β,γ -Unsaturated *o*-Hydroxyphenyl 1,2-Dimethylcyclopent-2-enyl ketone

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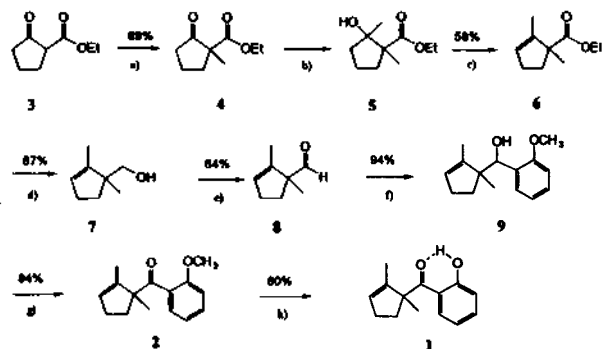
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The β,γ -UKs undergo virtually all types of photochemical processes known for isolated ketones or alkenes as well as two unique processes. The two particular processes result from the presence of an alkenyl group at the β,γ -position from a carbonyl chromophore in a single molecule: the [1,3] acyl shift (1,3-AS) and [1,2] acyl shift (1,2-AS) or oxa-di- π -methane (ODPM) rearrangement. Direct irradiation usually leads to a new rearranged β,γ -UK, which is the result of a 1,3-AS reaction. In contrast, triplet sensitized irradiation usually gives rise to a cyclopropyl ketone, the result of a 1,2-AS or ODPM rearrangement. With regard to the spin multiplicity and configuration of the state from which a reaction occurs, the n,π^* excited singlet state is believed to give the 1,3-AS product in most cases, whereas the 1,2-AS product comes from a $\pi-\pi^*$ triplet excited state.^{2a} It should be noted, however, that the observations about the photorearrangement mentioned above are only generalities and that the specific mechanism for any single ketone may deviate substantially from this simple, approximate description. Quite naturally, a fairly thorough study has been conducted on the substituent effect in β,γ -UKs to elucidate the exact nature of the mechanistic behavior of this interesting chromophore.² But the effect of a hydroxyl group positioned at the α -position to the carbonyl, that is believed to play a very crucial role in the polymer photochemistry of UV stabilizers, has not been studied. In the chemistry of light stabilizers such as *o*-hydroxybenzophenone and *o*-hydroxyphenylbenzotriazole, the light absorbing group capable of forming an intramolecular hydrogen bonding would funnel away the light energy absorbed by the chromophore.^{3a,b,4} Then one would say that the photochemical outcome of the introduction of a molecular geometry capable of forming a six-membered ring intramolecular hydrogen bonding would be the inactivation of the otherwise photoreactive group. Thus we have chosen two compounds, *o*-hydroxyphenyl 1,2-dimethylcyclopent-2-enyl ketone **1**, and *o*-methoxyphenyl 1,2-dimethylcyclopent-2-enyl ketone **2** to study the effect of intramolecular hydrogen bonding on the photochemistry of β,γ -UKs. By comparing the photochemistry of **1** and its non-hydrogen bonding analog **2**, we hoped to clarify the effect of

α -hydroxyl group on the photochemistry of β,γ -UKs.

The compounds **1** and **2** were chosen for this study because photorearrangement of this carbon skeleton, as a β,γ -unsaturated ketone, had well been established.⁵ Thus the comparison of the rearrangemental behavior could be made relatively easily with many other previously studied compounds.⁵ The other advantages of selecting this β,γ -UK carbon framework, except the ease of syntheses, was that 1,3-AS from the starting ketone **2**, if at all occurred, could readily be detected by NMR. Unlike the starting ketone, the products resulted from 1,3-AS of **1** and **2** would have no vinylic proton. This would help determine the structure of the 1,3-AS product easier. For synthesis, the method of Schaffner and coworkers^{5a} was adopted with several modification. Starting from ethyl 2-oxocyclopentanecarboxylate (**3**), the ester was methylated with $\text{CH}_3\text{I}/t\text{-BuOK}$ (**4**) and then converted to a hydroxy ester with a concomitant introduction of the second methyl group by Grignard reaction with CH_3MgI (**5**). Dehydration was followed to complete the formation of β,γ -alkene functionality (**6**). The ester group was then replaced to *ortho*-methoxy- or *ortho*-hydroxyphenyl ketone by sequential reactions of LAH reduction (**7**), oxidation by PDC (**8**), Grignard reaction (**9**), and the second oxidation with PDC. For demethylation at the last step, we have tried a few methods, but BBr_3 worked best as far as the yield and the neatness of the reaction were concerned. Thus the hydroxyphenyl β,γ -UK **1** was synthesized from ethyl 2-oxocyclopentanecarboxylate in 18% overall yield. The structures of all intermediary products along the synthetic schemes were positively identified by NMR and IR.⁶ The synthetic scheme is depicted in Scheme 1.

For direct irradiation of *o*-methoxyphenyl 1,2-dimethylcyclopent-2-enyl ketone **2**, the cyclohexane solutions of 0.01 M of **2** were put into Pyrex tubes and photolyzed in the Rayonet Photochemical Reactor using 16 RUL-350 lamps. Progress of the photolysis was followed and analyzed by GC using 30 m HP-1 column and octadecane as an internal standard. Photostationary state was reached in 1.5 h under our reaction condition, which composed of 63% of the starting ketone **2**, 8% of the 1,3-AS product **10**, 5% of an al-

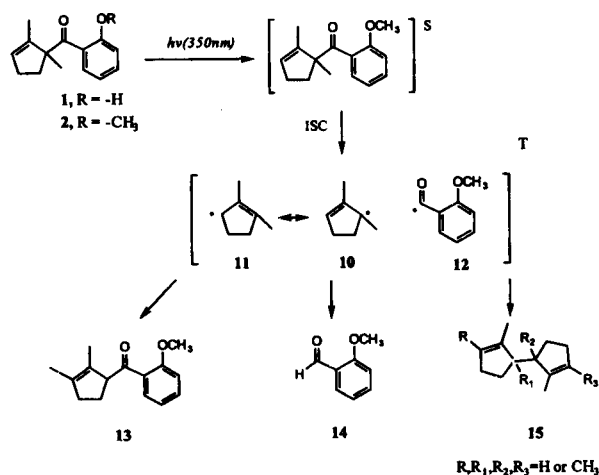


Scheme 1. Reagents and Conditions: a) *t*-BuOK/*t*-BuOH, CH₃I; b) CH₃MgI/Et₂O; c) *p*-TsOH/PhH, -H₂O; d) LiAlH₄/THF; e) PDC, AcOH, 3A molecular sieve; f) *o*-Bromoanisole, Mg/Et₂O; g) PDC, AcOH, 3A molecular sieve; h) BBr₃, -78 °C → r.t.

aldehyde 11, and 15% of the radical coupling product 12. An unknown amount of the unidentified products was also detected on GC. After photolysis, the solvent was removed and the products were separated by silica gel column chromatography. Structure identification was made for all three products by NMR and GC/MS.

The three photolysis products whose structures positively identified were another β,γ -UK 13, an aldehyde 14, and an alkene 15 in 27:16:57 ratio (Scheme 2). Supposing that the photochemical property of the methoxy β,γ -UK were similar to that of a typical acyclic aromatic β,γ -UK,^{5a} the first step in photolysis would be the homolytic α -cleavage to form radicals 10 and 12. Then we can safely assume that the alkene 15 would have resulted from the coupling of the two cyclopentenyl radicals 10 with 11, and the 1,3-AS product 13 from the aryl radical 12 and the rearranged cyclopentenyl radical 11, whereas the aldehyde 14 would have been formed from the abstraction of a hydrogen by the aryl radical 12, as illustrated in Scheme 2. Failure to discover the existence of ODPM product from 2 also underscored the fact that this β,γ -UK behaved similarly to the other acyclic aryl β,γ -UKs, in which no ODPM product formation had been observed on direct irradiation.

Quantum efficiencies were measured by the benzophe-



Scheme 2.

none-benzohydrol method.⁷ The relative quantum efficiency of disappearance of the starting ketone 2 was 0.81 and those of appearance of the 1,3-AS product ketone 13, aldehyde 14, and the allylic radical coupling product alkene 15 were measured to be 0.17, 0.10, and 0.35, respectively. Several workers have reported the quantum efficiencies of each photochemical process for analogous cyclopentenyl β,γ -UK to our ketone 2.^{5c} In these instances, quantum efficiencies of formation of the products were 0.14-0.16 and that of disappearance of the starting β,γ -UK ranged 0.52-0.64. These values suggest that the photoreactivity of our ketone 2 quite resembles any other aryl cyclopentenyl β,γ -UKs.

Unlike its methoxy analog, the hydroxy β,γ -UK 1 stubbornly resisted the photolysis. Only the starting ketone 1 was recovered even after 2 hours of irradiation with sixteen 15 W RUL-350 lamps in cyclohexane. This might support the fact the hydroxyl group which can form an intramolecular hydrogen bonding with a carbonyl oxygen in the β,γ -UK inhibits the β,γ -UK photochemistry very efficiently. This postulate was at least qualitatively confirmed. The hydroxy ketone 1 showed somewhat increased reactivity in more polar or protic solvents, in which the degree of intramolecular hydrogen bonding was diminished. When the hydroxy ketone 1 was irradiated in acetonitrile or in methanol with sixteen 350 nm UV lamps for 2 hours, 5.5-10% of the starting ketone 1 was converted to several unidentified products.

In conclusion, we have demonstrated that the hydroxyl group strategically positioned so as to form an intramolecular hydrogen bonding in β,γ -UK blocks the photochemical pathways of the β,γ -unsaturated ketone chromophore.

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6. The proton NMR data (Bruker AC-100, CDCl_3 , δ) of the key intermediary products are as follows; for **1**, 1.3 (3H, s), 1.6 (3H, m), 2.3 (5H, m), 5.5 (1H, br.s), 6.8 (2H, m), 7.3 (1H, m), 8.1 (1H, dd), 12.6 (1H, s); **2** 1.3 (3H, s), 1.6 (3H, m), 2.4 (4H, m), 3.8 (3H, s), 5.5 (1H, br.s), 6.9 (3H, m), 7.3 (1H, m); **6**, 1.2 (3H, t), 1.3 (3H, s), 1.5 (3H,

m), 2.3 (4H, m), 4.1 (2H, q), 5.4 (1H, br.s); and **8**, 1.2 (3H, s), 1.6 (3H, m), 2.3 (4H, m), 5.6 (1H, br.s), 9.4 (1H, s).

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Asymmetric Metal-Insulator Transitions and Low Magnetic Field Giant Magnetoresistance of $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.35 \leq x \leq 0.5$)

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The giant magnetoresistance (GMR) properties of mixed valent perovskite-type manganese oxides are attracting wide attention partly due to the hope of developing better MR materials.¹⁻⁴ However, despite the impressively large MR values, most of known compounds of this class has significant demerits for such applications. They generally require very strong magnetic fields to exhibit significant MR effects and the temperatures for the maximum MR are usually far below room temperature. The first problem is considered to be more serious for realization of manganese oxide based MR devices.^{1-3,5-7}

Previously, we have studied many perovskite type manganese oxides for their electrical properties and have related their metal-insulator (MI) transitions to the lattice distortions created by the A-site cation sizes of the general formula ABO_3 .⁸ During this work, we found that compounds in the $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ system had asymmetric peaks in the resistivity vs. temperature plots with sharp changes of resistivity with temperature below T_{MI} 's. Since application of magnetic field raises T_{MI} and thereby lowers the resistivity particularly at around T_{MI} , we thought that such sharp transitions would result in large MR ratios.

Recently, Tokura *et al.* reported a lattice striction coupled MR in a perovskite type $(\text{Nd}_{1-y}\text{Sm}_y)_{1/2}\text{Sr}_{1/2}\text{MnO}_3$ ($y=0.938$) single crystal.⁹ This compound exhibits simultaneous ferromagnetic ordering, MI transition and lattice shrinkage at T_{MI} . The resistance rises almost vertically with temperature by an order of 10^3 ohm-cm just below T_{MI} , and consequently, this compound shows a large MR effect of almost 100% under as low applied field as 0.25 T. Similar MI transitions are observed in the other members of the solid solution but with much reduced sharpness and higher T_{MI} as the Nd content increased.¹⁰ Therefore, we suspected that the Sm ion, probably due to its size coupled with that of Sr, plays a crucial role in displaying the sharp MI-transitions in these compounds.

Tomioka *et al.* studied the MR behavior of $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$.^{11,12} This compound shows almost the same feature as $(\text{Nd}_{1-y}\text{Sm}_y)_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ ($y=0.938$) but somewhat less drastically. A study on $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x=0.33$ and 0.40 shows

that these also have rather sharp MI-transitions and $x=0.2$ and 0.55 compounds show semiconducting behavior to the low temperature.^{13,14} However, there has been no systematic studies on this system. In this paper, we report the MI transitions in the $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.35 \leq x \leq 0.5$) series and the low field MR properties of the $x=0.4$ member.

$\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0.35, 0.375, 0.40, 0.425, 0.45, 0.475, 0.5$) samples were prepared by calcining stoichiometric mixtures of Sm_2O_3 , SrCO_3 and Mn_2O_3 at 1000 °C for 10 hour and sintered at 1450-1500 °C for 50-100 hour in air. The single phase nature of the samples were confirmed by indexing their X-ray powder patterns by orthorhombic perovskite structures with the space group Pbnm. The resistance and the magnetization data were obtained by the standard four probe method and on a SQUID magnetometer, respectively.

Figure 1 shows the temperature dependency of resistivity of the compounds in the $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ system. All the samples in the x -range studied in this study exhibited sharp MI transitions similar to those of $(\text{Nd},\text{Sm})_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. T_{MI} values varied with x peaking at $x=0.45$ with 135 K close to the reported value of about 125 K.^{11,12} The peak shape in the resistivity vs. temperature plot for $x=0.4$ member is most asymmetric with a steep rise and a gradual decrease with increasing temperature just below and above T_{MI} , respectively. Tokura *et al.*⁹ attributed the asymmetric peaks in their $(\text{Nd},\text{Sm})_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ samples to the first order transition with charge ordering which is often found in other perovskite oxides particularly with the oxidation state of +3.5 for Mn. In their study, however, there was no evidence provided to prove the occurrence of charge ordering. However, our data show that the asymmetric nature of the resistivity vs. temperature does not necessarily have to accompany any particular Mn oxidation state. In fact, as x approaches 0.5 beyond 0.45 the peak shape becomes more symmetric (Figure 1). We believe the asymmetry comes from a certain type of lattice distortion due to the A-site cations.

Since we were seeking a compound with both high T_{MI} and a highly asymmetric MI transition peak, we have