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Photochemistry of 1-(*o*-Tolyl)-1-benzoylcyclopropane and 2-(*o*-Tolyl)-2-benzoyloxirane: Determination of Ring Opening Rates of Oxiranylcarbinyl Radicals[1]

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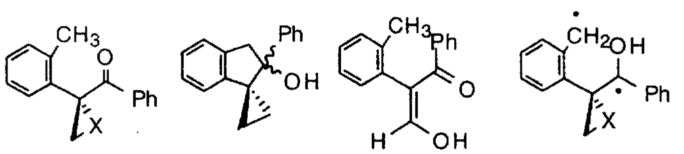
Abstract: *Photolysis of the title compounds results in efficient hydrogen transfer reaction to produce 1,5-biradical intermediate, which does not form in the photolysis of a structurally similar compound, α-(o-tolyl)isobutyrophenone. From their kinetic studies we have measured the rearrangement rate constant of a substituted oxiranylcarbinyl radical.* © 1999 Elsevier Science Ltd. All rights reserved.

Cyclopropylcarbinyl and oxiranylcarbinyl radical rearrangements have extensively exploited in synthetic organic chemistry. As design in organic synthesis using radical chemistry requires well-understanding of reaction rates, kinetic studies on rearrangement are essential. Even though kinetic data for the rearrangement of parent and substituted cyclopropylcarbinyl radical system have quite been accumulated, the corresponding data for oxiranylcarbinyl radical rearrangement have been only a few up to now mainly because it is known to occur very fast. Gleicher has assigned a lower limit for the rate of oxiranylcarbinyl radical ring opening at 1×10^{10} s^{-1} at 70°C using competitive reactions of a cyclopropyloxiranylmethyl radical.[2] More recently, Rawal reported the rate constant of 3.2×10^{10} s^{-1} at 25-30°C for a cyclohexyl-substituted oxiranylcarbinyl radical, a tertiary radical, using a radical clock method.[3] Theoretical studies also showed that the reaction barrier is very low.[4] In the course of our studies on the photochemistry of α-(*o*-alkylphenyl)acetophenones with small rings conjugated with carbonyl group, we have found that the title compounds can be good models to study kinetics of cyclopropylcarbinyl and oxiranylcarbinyl radical rearrangement. Here we report our preliminary findings that allow us to measure directly the rate constants of rearrangements.



1a X = CH$_2$
1b X = O

2

3

1a-BR X = CH$_2$
1b-BR1 X = O

Scheme 1.

The ketones of **1a** and **1b** in Scheme 1 were synthesized from α-methylidene-α-(*o*-tolyl)acetophenone by standard procedures.[5] Irradiation of **1a** (0.01 M) in benzene with the output of a medium pressure mercury arc lamp filtered by Pyrex resulted in clean photocyclization to **2**.[6] The photoproduct was stable under the irradiation condition. No other products were detected in the ^{1}H NMR spectrum of the crude reaction mixture. Quantum yield of formation of **2** was determined to be 0.14 in benzene by parallel irradiation with valerophenone as an actinometer.[7] Irradiation of **1b** under the same

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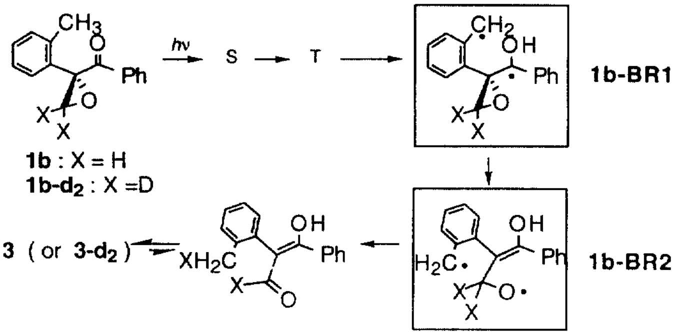
condition yielded **3**.[8] The quantum yield of this reaction was 0.05 in benzene. If the irradiation continued for extended periods, a complex mixture of products was observed, which presumably resulted from a secondary photoreaction of the initially formed products.

In both reactants, no α-cleavage products were detected. α-(*o*-Tolyl)isobutyrophenone, which is closely resembled to **1a** structurally, is known to form only α-cleavage products.[9] Presumably the bond between the cyclopropyl (or oxiranyl) and carbonyl is strengthened by the orbital overlap of the bent orbitals of the three membered ring with π orbitals of the neighboring carbonyl group, which retarded the α-cleavage reaction and makes the competing Norrish/Yang reaction pathway[10] prevail.

The formation of **3** from **1b** can be explained by two different mechanisms. One is the reaction pathway that has frequently been cited in the photochemistry of conjugated oxiranyl ketones.[11] The reaction mechanism involves the ring opening and 1,2-hydrogen shift, which have been suggested to occur almost simultaneously from n, π* excited states. The other possible mechanism is hydrogen abstraction, oxiranyl ring opening, followed by hydrogen atom shift as shown in Scheme 2. Considering **1a**, that is almost identical to **1b** geometrically, gives 1,5-biradical intermediate *via* hydrogen abstraction, it seems reasonable to propose such a mechanism.



Scheme 2.

In order to see which mechanism is operating in the photoreaction of **1b**, we have prepared and irradiated **1b-d$_2$** under the same irradiation condition. The ^1H NMR spectrum of the photoproduct from **1b-d$_2$** was essentially the same as that of **3** except that the peak at 16.02 ppm became singlet and that the peak at 8.59 ppm was missing. In addition, the peak at 2.02 ppm became broadened, which implicated the incorporation of a deuterium into a benzylic methyl group. It was further evidenced in its ^{13}C NMR spectrum showing a triplet with an equal intensity at 20.2 ppm. Accordingly, the compound was assigned as **3-d$_2$**. The result is consistent with the mechanism shown in Scheme 2.

More direct evidences have been obtained on the photochemical reaction mechanisms of **1a** and **1b** with a laser flash photolysis spectrometer. Samples of **1a** and **1b** were excited by 266 nm pulses of 8 mJ and 6 ns from a Q-switched Nd:YAG laser (Quanta System, HYL-101). Time-resolved transient absorption spectra were measured by monitoring emission from organic dyes excited by the same laser with a CCD (Princeton Instruments, ICCD-576-G) attached to a 0.5 m spectrometer (Acton Research, SpectraPro-500). The 1,5-biradical of **1a**, **1a-BR**, is attributable to the transient absorption spectrum of Figure 1(a) with the lifetime of 20 ns. The spectrum contains the absorption band of benzyl radical with the peak at 320 nm and that of a hydroxybenzyl radical with the peak at 350 nm.[12] However, the transient absorption of **1b** with the lifetime of 25 ns is much stronger and shifted to the blue with the lowest peak at 330 nm compared with that of **1a**. We ascribe this transient absorption mainly to the biradical of **1b-BR2** and the absorption band of 330 nm peak to the olefin conjugated with phenyl and benzyl radical chromophores, for the maximum absorption wavelength and the large extinction coefficient resemble those of stilbene. The absorption band of the benzyl chromophore of **1b-BR2** is buried under the strong absorption band with the peak at 330 nm. As the transient absorption resulting from **1b-BR1** decays too fast to measure directly with the spectrometer of 6 ns temporal resolution, we can only simulate its spectrum as iii in Figure 1(b) based on the assumption that the transient absorption spectrum at 2 ns contains more contribution from the fast decaying **1b-BR1** than that at 20 ns. Nevertheless, the fact that the spectrum iii displays the disappeared absorption band of hydroxybenzyl radical chromophore exposes that upon absorption of a photon **1b** undergoes intramolecular hydrogen transfer from the methyl group to the carbonyl group to yield the biradical of **1b-BR1** and then follows ring opening to form the biradical of **1b-BR2**.

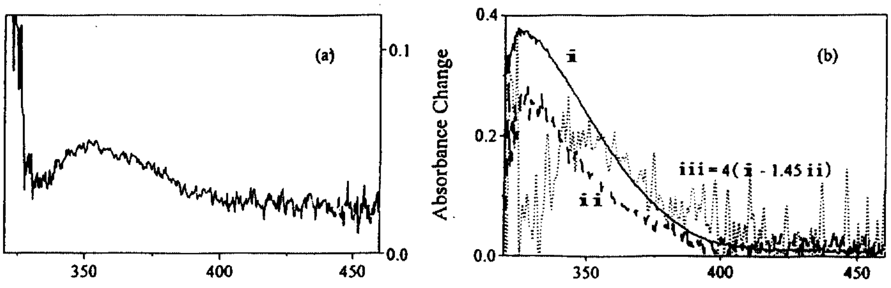


Figure 1. Time-resolved transient absorption spectra of 5×10^{-3} M cyclohexane solutions of **1a** at 20 ns after excitation (a) and **1b** at 2 ns (i) and 20 ns (ii) (b), The iii, simulated from 4(i-1.45ii), in (b) is the transient absorption spectrum of **1b** corresponding to that of **1a** in (a).

The transients bringing out the spectra of Figure 1 are not quenched by the presence of triplet quenchers such as conjugated dienes. However, they are quenched by methyl viologen cation to give birth to a new absorption band of reduced methyl viologen cation with the peak at 610 nm. These support that the transient absorption spectra of Figure 1 arise from biradicals rather than **1** at the lowest triplet state.[12b,13] We have also measured the intramolecular hydrogen transfer time of **1** as 0.5 ns and the ring opening time of **1b-BR1** as 1.8 ns by employing a picosecond streak camera (Hamamatsu. C2830) and a mode-locked Nd:YAG laser (Quantel, YG501). Kinetics of **1a** and **1b** are summarized in Scheme 3.

$$\mathbf{1a} \xrightarrow{h\nu} S_1 \longrightarrow T_1 \xrightarrow{0.5\text{ ns}} \mathbf{1a\text{-}BR} \xrightarrow{20\text{ ns}} \mathbf{2}$$

$$\mathbf{1b} \xrightarrow{h\nu} S_1 \longrightarrow T_1 \xrightarrow{0.5\text{ ns}} \mathbf{1b\text{-}BR1} \xrightarrow{1.8\text{ ns}} \mathbf{1b\text{-}BR2} \xrightarrow{25\text{ ns}} \mathbf{3}$$

Scheme 3.

Our results indicate that the biradical intermediate from **1a** cyclizes before the cyclopropyl ring opening, but that the oxiranyl ring opens up immediately after the initial hydrogen abstraction. The rate constant for the cyclopropylmethyl radical ring opening was reported as 1×10^8 s^{-1} at 25 °C by Newcomb[14] and the corresponding rate for the oxiranylcarbinyl radical is faster than this by two orders of magnitude.[1,2] The rearrangement may be much slower for 1-phenyl-1-hydroxy substituted system than the parent system. In fact, it has been known that benzyllic stabilization perturbs the equilibrium of the cyclopropylcarbinyl radical rearrangement[15] and that the conjugation of oxygen lowers the rate even further down.[16] Our laser flash photolysis experiment shows that the cyclopropyl ring opening of **1a-BR** does not occur in the time scale of 20 ns. The ring opening rate of 1-phenyl-1-hydroxy oxiranylcarbinyl radical is determined to be 5.6×10^8 s^{-1} from the biradical lifetime of 1.8 ns.

In summary, photolysis of the title compounds resulted in efficient hydrogen transfer reaction to produce 1,5-biradical intermediate, which was not observed in the photolysis of a structurally similar compound, α-(*o*-tolyl)isobutyrophenone. Photoreactivity of **1a** can be exploited to synthesize spiroindanol derivatives and the formation of **3** from **1b** shows a nice example of the oxiranylcarbinyl radical rearrangement induced by photochemical hydrogen abstraction. Kinetic studies using laser photolysis experiment allowed us to measure the rate constant of the rearrangement of a substituted oxiranylcarbinyl radical.

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6. Spectroscopic data of **2:** ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.65-6.75 (m, 9H), 3.83, 3.43 (AB quart, 2H, J = 16.8 Hz), 2.41 (s, 1H, -OH), 1.20-0.59 (m, 4H); ^{13}C NMR (CDCl$_3$, 56 MHz) δ 146.5, 144.1, 140.6, 128.4, 127.8, 127.4, 126.9, 126.6, 125.2, 119.6, 84.2, 50.2, 39.8, 18.9, 11.0. IR (KBr) 3553, 1485 cm^{-1}. EI MS 236 (M$^+$, 29.3), 218 (14.7), 208 (42.0), 105 (100), 77 (33.3).
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