PHOTOCHEMISTRY OF γ-ALLENYL-SUBSTITUTED CONJUGATED ALKYLIDENECYCLOALKANONES

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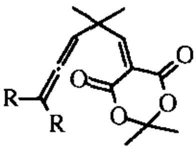
Abstract —— The photolyses of the γ-allenyl-substituted conjugated alkylidenecycloalkanones underwent the intramolecular *oxa*-Diels-Alder reaction and the *E*-*Z* geometrical isomerization, and for the cyclopentanone possessing a 3-methyl-1,2-butadienyl group, the intramolecular [2+2] cycloaddition also occurred. The *oxa*-Diels-Alder reaction takes place *via* photochemical process of the *Z*-enones.

The photochemical intramolecular [2+2] cycloaddition of cycloalkenones linked to an alkene by hydrocarbon chains is well-known, has been extensively investigated and is a useful reaction in organic synthesis.[1] It has been reported that the divinyl methanes in which one vinyl group is conjugated with carbonyl group, in the photolyses, undergo both a di-π-methane rearrangement and an intramolecular [2+2] cycloaddition.[2] An allene is a good alkene that undergoes the photochemical intramolecular [2+2] cycloaddition to cycloalkenones.[3] The photochemistry of these allenic compounds has been studied based on the length of the side chain, linkage position on the cycloalkenone, temperature, and the ring size effect. However, there is no report on the photochemistry of allenyl-cycloalkenonylmethanes. The direct photolyses of the allenyl-styryl-[4] and allenyl-alkenoylmethanes[5] undergo the [2+2] cycloaddition mainly. Recently, we reported that the cyclic acylals (**1**) possessing the allenyl group at the γ-position form an intramolecular CT complex between the allenyl and vinyl groups, whose direct photolysis produced the alkenylidenecyclopropane as the main product with a proton or hydrogen transfer *via* the CT excited state, whereas the acetone-sensitized photolysis yielded the [2+2] cycloadduct.[6] Furthermore, for the diesters (**2**), the intramolecular [2+2] cycloaddition occurred mainly in both the direct and acetone-sensitized photolyses.[7]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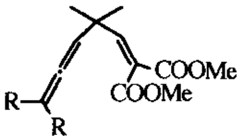
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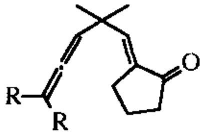
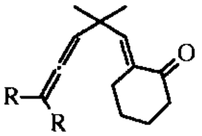
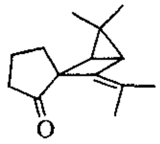

3a: R=Me
b: R=H


4a: R=Me
b: R=H

Thus we became interested in studying the photochemistry of allenyl-cycloalkenonylmethanes. We would like to report herein the results obtained from the photolyses of γ-allenyl-substituted alkylidenecycloalkanones[8] (**3a**, **3b**, **4a**, and **4b**) which are the *exo*-cycloalkenones.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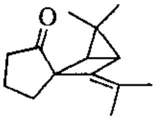
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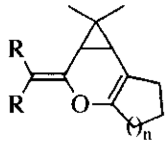

7a: R=Me, n=1
b: R=H, n=1
10: R=H, n=2

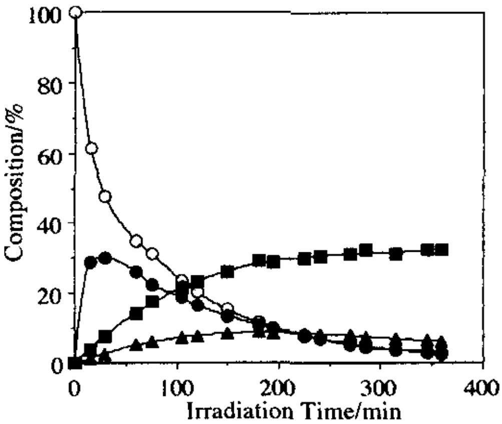
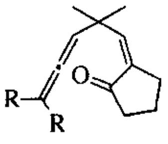
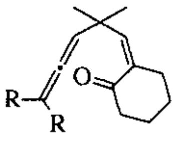
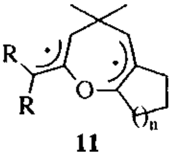


Figure 1. Composition of the isomer mixture vs. irradiation time for isomerization of **3a** (0.01 mol dm^{-3}; ○) to **5+6** (■), **7a** (▲), and **8a** (●).


8a: R=Me
b: R=H


9a: R=Me
b: R=H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A solution of the enone (**3a**: 0.01 mol l^{-1}) in hexane (400 ml) was irradiated for 6 h using a 100-W high-pressure mercury lamp with a Pyrex jacket at room temperature under an argon atmosphere. After evaporation of the solvent, photoproducts were isolated by medium-pressure silica gel chromatography using hexane/ether as an eluent to give **5**, **6**, **7a**, and **8a** in 17%, 11%, 6%, and 5% yields, respectively, and **3a** was recovered (3%). The structures of these photoproducts were determined by their spectroscopic properties.[9] Quantum yields for the isomerization of **3a** to the photoproducts at 313 nm[10] under an argon atmosphere in hexane are as follows: $\Phi_{3a\rightarrow5+6}=0.011$, $\Phi_{3a\rightarrow7a}<0.001$, $\Phi_{3a\rightarrow8a}=0.19$, whereas those of **8a** are as follows: $\Phi_{8a\rightarrow5+6}=0.010$,

$\Phi_{8a\rightarrow7a}$=0.0072, $\Phi_{8a\rightarrow3a}$=0.15. As shown in Figure 1,[11] it is found that there is an induction period for the formation of **7a**. When a solution of **8a** in hexane was allowed to stand at room temperature in the dark, no *oxa*-Diels-Alder reaction occurred. Hence, it has become apparent that the dihydropyran (**7a**) was derived from the photochemical *oxa*-Diels-Alder reaction of the (*Z*)-form (**8a**). The isolated *endo*-form (**6**) was found to be readily rearranged to the *exo*-form (**5**).[12] On the other hand, a similar photolysis of **3b** in hexane led to a dihydropyran (**7b**; 25%) and a (*Z*)-form (**8b**; 8%), but [2+2] cycloadducts were not obtained. A similar result for the formation of **7b** was also obtained from the course of the photoreaction of **3b** and from the quantum yields ($\Phi_{3b\rightarrow7b}$<0.001, $\Phi_{8b\rightarrow7b}$= 0.049).[13]

For similar direct photolysis cases of **4a** and **4b** in hexane, the *E-Z* geometrical isomerization mainly occurred and these geometrical isomers were observed in an *ca. E:Z*=1:9 ratio as a steady state. Upon irradiation for 1 h, (*Z*)-isomers (**9a** and **9b**) were obtained both in 51%. During the prolonged irradiation of **4a**, compositions of **4a** and **9a** gradually decreased due to their polymerization and the formation of complicating compounds, which might involve the [2+2] cycloadducts and dihydropyran from **4a** and/or **9a**, but those were not separately isolated. Moreover, although the polymerization was found after the prolonged irradiation (18 h) of **4b**, the dihydropyran (**10**) was also obtained (6%). Quantum yields for these isomerization in hexane are as follows: $\Phi_{4a\rightarrow9a}$=0.34; $\Phi_{4b\rightarrow9b}$=0.29, $\Phi_{4b\rightarrow10}$<0.001; $\Phi_{9a\rightarrow4a}$=0.10; $\Phi_{9b\rightarrow4b}$=0.14, $\Phi_{9b\rightarrow10}$=0.012.

Acetophenone was a good sensitizer in these reactions using a 313 nm radiation source ($\Phi_{3a\rightarrow5+6}$=0.012, $\Phi_{3a\rightarrow7a}$<0.001, $\Phi_{3a\rightarrow8a}$=0.22; $\Phi_{3b\rightarrow7b}$<0.001, $\Phi_{3b\rightarrow8b}$=0.27; $\Phi_{8a\rightarrow5+6}$=0.038, $\Phi_{8a\rightarrow7a}$=0.0084, $\Phi_{8a\rightarrow3a}$=0.22; $\Phi_{8b\rightarrow7b}$=0.014, $\Phi_{8b\rightarrow3b}$=0.32; $\Phi_{4a\rightarrow9a}$=0.26; $\Phi_{4b\rightarrow9b}$=0.26, $\Phi_{4b\rightarrow10}$<0.001; $\Phi_{9a\rightarrow4a}$= 0.053; $\Phi_{9b\rightarrow4b}$=0.080, $\Phi_{9b\rightarrow10}$=0.017). However, when isoprene was used as a quencher, it was ineffective in these photolyses. Therefore, although these isomerizations of the enones under direct irradiation occur from the singlet excited state, they are possible from the triplet.

The *oxa*-Diels-Alder reaction during the photolyses of the enones requires structural overlap between the carbonyl oxygen and the allene center carbon, hence the excited carbonyl oxygen of the enones will attack the allene center carbon to yield a biradical intermediate such as **11**, followed by ring closure giving the dihydropyrans. On the other hand, the π-π^* and n-π^* transitions of the (*E*)-enones (**3a**, **3b**, **4a**, and **4b**) in the uv-absorption spectra exhibit absorption maxima at *ca.* 245 nm and 350 nm, respectively, while n-π^* transitions of the five-membered (*Z*)-enones (**8a** and **8b**) show more bathochromic shifts (*ca.* 30 nm) than those of the six-membered (*Z*)-enones (**9a** and **9b**).[14] Furthermore, the extinction coefficient in the π-π^* range of about 250 to 300 nm of the enones

(**3a**, **4a**, **8a**, and **9a**) are somewhat larger than those of **3b**, **4b**, **8b**, and **9b**. This indicates that the CT interaction between the allenyl and vinyl groups of **3a**, **4a**, **8a**, and **9a** by an electron donating methyl group linked to the allene is larger than that of the corresponding propadienylenones (**3b**, **4b**, **8b**, and **9b**). Such a tendency of the uv-absorption spectra suggests that **3a** and **8a** are susceptible to intramolecular [2+2] cycloaddition in comparison to **3b** and **8b**. However, it is not understood why the six-membered enones (**4a** and **9a**) possessing a 3-methyl-1,2-propadienyl group did not give the [2+2] cycloadducts and the dihydropyran by uv-irradiation. From a PM3 molecular orbital calculation,[15] a torsion angle about the *s-cis* C=C-C=O single bond in the *exo*-six-membered enones is *ca.* 70°, while the five-membered moieties are nearly coplanar. Consequently, it seems likely that the intramolecular [2+2] cycloaddition and the *oxa*-Diels-Alder reaction of the enones subject to considerable steric hindrance by differences in the ring structure and of the allenyl group. Although the allenes have been recently employed as useful dienophiles for dienes or heterodienes in the thermal Diels-Alder reaction,[16] such photochemical intramolecular *oxa*-Diels-Alder reactions of the enone with the allene is the first example.[17,18]

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9. **5**: ir (neat) 1734, 1640 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.97(3H, s), 1.20(3H, s), 1.45(3H, s), 1.50(1H, d, *J*=5.2 Hz), 1.67(3H, s), 1.7-2.5(7H, m); ^{13}C nmr ($CDCl_3$) δ 18.6(q), 18.8(q), 19.0(q), 19.2(t), 24.1(q), 26.7(s), 31.8(d), 31.9(t), 34.6(d), 38.4(t), 56.5(s), 121.1(s), 133.7(s), 221.0(s). Hrms Found *m/z* 204.1506. Calcd for $C_{14}H_{20}O$: M, 204.1515. **6**: ir (neat) 1736, 1628 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.91(3H, s), 1.28(3H, s), 1.45(3H, s), 1.60(3H, s), 1.67(1H, d, *J*=5.3 Hz), 1.9-2.5(7H, m); ^{13}C nmr ($CDCl_3$) δ 17.9(t), 18.2(q), 18.6(q), 19.4(q), 24.9(q), 28.8(s), 32.6(d), 36.2(t), 36.5(d), 36.8(t), 55.6(s), 123.8 (s), 130.7(s), 217.2(s). Hrms Found *m/z* 204.1475. Calcd for $C_{14}H_{20}O$: M, 204.1515. **7a**: ir (neat) 1703 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 0.76(3H, s), 1.1-2.5(13H, m, including 2Me as singlet at 1.19 and 1.70 ppm), 2.2-2.5(4H, m); ^{13}C nmr ($CDCl_3$) δ 15.5(q), 16.6(q), 18.8(q), 19.5(t), 22.8(d), 23.4(d), 25.1(s), 26.6(q), 30.4(t), 31.8(t), 104.8(s), 108.7(s), 141.0(s), 147.9(s). Hrms Found *m/z* 204.1492. Calcd for $C_{14}H_{20}O$: M, 204.1515. **8a**: ir (neat) 1969, 1717, 1625 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 1.27(6H, s), 1.68(6H, d, *J*=2.6 Hz), 1.7-2.1(2H, m), 2.2-2.4(2H, m), 2.5-2.7(2H, m), 5.38(1H, septet, *J*=2.6 Hz), 5.99(1H, t, *J*=2.3 Hz); ^{13}C nmr ($CDCl_3$) δ 20.5(t), 20.8(2C, q), 28.3(2C, q), 34.0(t), 37.2(s), 41.0(t), 97.3(s), 98.8 (d), 135.5(s), 148.0(d), 199.2(s), 206.0(s). Hrms Found *m/z* 204.1506. Calcd for $C_{14}H_{20}O$: M, 204.1515.
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