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Photochemical α-Cleavage Reaction of Levoglucosenone

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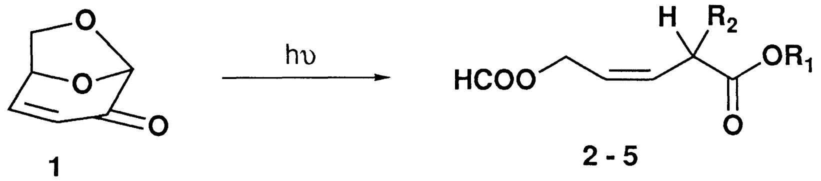
Irradiation of levoglucosenone having a 6-membered cyclic α,β-unsaturated ketone structure with a high pressure mercury arc stereoselectively produced (*Z*)-β,γ-unsaturated acid derivatives. The mechanism of the formation of these products is explained in terms of the α-cleavage reaction which is scarcely observed in the photochemical reaction of α,β-unsaturated ketones.

Photochemical reactions of cyclic α,β-unsaturated ketones have been widely investigated, and a variety of products are known to be generated through reactions such as rearrangement, dimerization, addition, isomerization, and so on.1) However, α-cleavage scarcely occurs during the photolysis of α,β-unsaturated cyclic ketones,2,3) in spite of being one of the typical photochemical reactions for saturated cyclic ketones.4) In particular, for 6-membered cyclic α,β-unsaturated ketones, no example of the α-cleavage reaction has been reported except for McMurry's study.5) They reported that the photolysis of 6-hydroxy-4,4-dimethylcyclohexenone gave α-cleavage products in 7.8% yield and the reaction proceeded *via* the singlet excited state. Here we describe that the irradiation of levoglucosenone,6) which has a 6-membered cyclic α,β-unsaturated ketone structure, leads to α-cleavage *via* the triplet excited state and stereoselectively affords (*Z*)-β,γ-unsaturated acid derivatives in high yields.

Irradiation of levoglucosenone (**1**) (4.0 mmol) in methanol (40 ml) using a 500 W high pressure mercury arc through a Pyrex filter for 30 h afforded a 99:1 mixture of methyl (*Z*)- and (*E*)-5-formyloxy-3-pentenoate (**2**)7) in 75% isolated yield (Table 1). When the photolysis was carried out in hydrous benzene or t-butyl alcohol, the corresponding acid **3** or ester **4** was produced, respectively. The acid **3** was readily transformed into 3,6-dihydro-2H-pyran-2-one8) (**6**) by treatment with 4-toluenesulfonic acid in 71% yield; the structure and

Table 1. Photochemical reaction of levoglucosenone



1

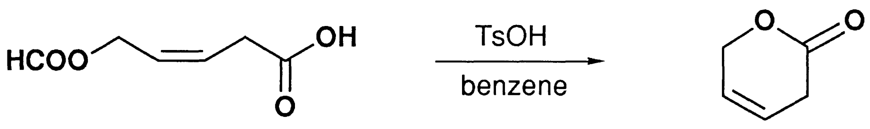
2 - 5

2 : R_1 = Me, R_2 = H
3 : R_1 = H, R_2 = H
4 : R_1 = t-Bu, R_2 = H
5 : R_1 = Me, R_2 = D

Solvent	Additive	Time / h	Product	Yield / %[a]	*E* / *Z*[b]	Recovery / %[a]
MeOH	none	30	**2**	58	1 / 99	15
"	acetophenone[c]	6	**2**	64	22 / 78	10
Benzene/H_2O	none	30	**3**	75	4 / 96	0
"	acetophenone[c]	6	**3**	75	59 / 41	0
t-BuOH	none	30	**4**	44	1 / 99	8
"	acetophenone[c]	6	**4**	45	45 / 55	8
"	benzaldehyde[c]	6	**4**	45	12 / 88	2
"	benzophenone[c]	10	**4**	40	1 / 99	14

a) Isolated yield. b) Determined by 400 MHz ^1H NMR. c) 1 equiv. sensitizer was used.

the stereochemistry of **3** were thus confirmed to be that of the (*Z*)-β,γ-unsaturated acid derivative. The photolysis of **1** in CH_3OD instead of methanol was examined to explore the intermediate in this reaction. From the ^1H-NMR and mass spectral study of the product **5**, deuterium was ascertained to be incorporated into the 2-position. The result suggests that an α,β-unsaturated ketene is a possible intermediate.

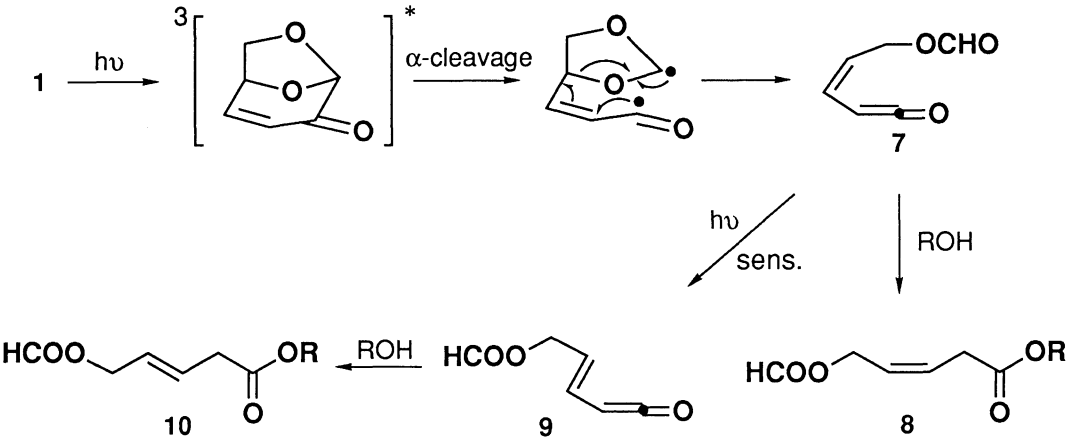


3

6

The sensitization experiments were performed to elucidate the reaction mechanism. The reaction was sensitized by acetophenone, benzaldehyde, and benzophenone as shown in Table 1. However, the stereoselectivity was remarkably decreased in the presence of acetophenone or benzaldehyde but was retained in the presence of benzophenone. From these results, it is apparent that the reaction proceeds *via* the triplet excited state.

A pathway which accommodates the foregoing results is outlined in Scheme 1. Thus, the diradical generated by the α-cleavage of **1** *via* the triplet excited state rearranges to an intermediary (Z)-ketene **7**, which is suffered by addition of a solvent such as H_2O, methanol, or t-butyl alcohol to give acid or esters **8**. When the irradiation is made in the presence of acetophenone or benzaldehyde, the intermediate **7** is partly isomerized to the (*E*)-ketene **9**, which also reacts with the solvent to yield the corresponding isomeric acid or esters **10**.9) On the other hand, benzophenone acts as a sensitizer not for the *E*/*Z* isomerization of **7** but for the α-cleavage of levoglucosenone. These results suggest that the triplet excited energy of the (Z)-ketene **7** is higher than that of benzophenone and lower than that of acetophenone and benzaldehyde.



Scheme 1.

The selective formation of the α-cleavage products seems to depend on two factors; the stability of the acetal radical generated by the α-cleavage, which is stabilized by two oxygen atoms, and the strain which is ascribed to the dioxabicyclo[3.2.1]hexenone structure of levoglucosenone.

The synthetic application of this reaction and the substituent effect for the α-cleavage reaction of cyclic α,β-unsaturated ketones are now in progress.

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References

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2) D. I. Schuster, *Pure Appl. Chem.*, **41**, 601 (1975); D. I. Schuster, "Rearrangements in the Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 3, Chap. 17.

3) For 5-membered cyclic α,β-unsaturated ketones, It has been known that only cyclopentenones substituted at 5-position produced α-cleavage products. W. C. Agosta and A. B. Smith, III, *J. Am. Chem. Soc.*, **93**, 5513 (1971).

4) P. J. Wagner, "Rearrangement in the Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 3, Chap. 20.

5) M. Jeffares and T. B. H. McMurry, *J. Chem. Soc., Chem. Commun.,* **1976**, 793.

6) Systematic name: 1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose.

7) Spectroscopic data for **2** was typically given as follows: IR (neat) 1731, 1725, 1167 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$) δ 3.21 (d, J = 7.32 Hz, 2H), 3.71 (s, 3H), 4.72 (d, J = 6.83 Hz, 2H), 5.77 and 5.87 (each m, each 1H), 8.07 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 32.85, 52.05, 59.36, 126.21, 126.75, 160.75, 171.38; MS *m/z* (relative intensity) 159 (M^++1, 9.0), 158 (0.2), 127 (15.1), 113 (100), 98 (42.4), 81 (31.9), 71 (69.4); HRMS calculated for $C_7H_{10}O_4$ *m/z* 158.0586, found 158.0593.

8) R. A. Ruden, R. Bonjouklian, *J. Am. Chem. Soc.*, **97**, 6892 (1975).

9) The isomerization of **8** may occur to give the (*E*)-esters or acid **10** under the sensitization conditions, which was suggested by a referee.

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