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PHOTOINDUCED OXIDATIVE CLEAVAGE OF ARYLCYCLOPROPANES IN THE PRESENCE OF ORGANIC ELECTRON-ACCEPTOR1)

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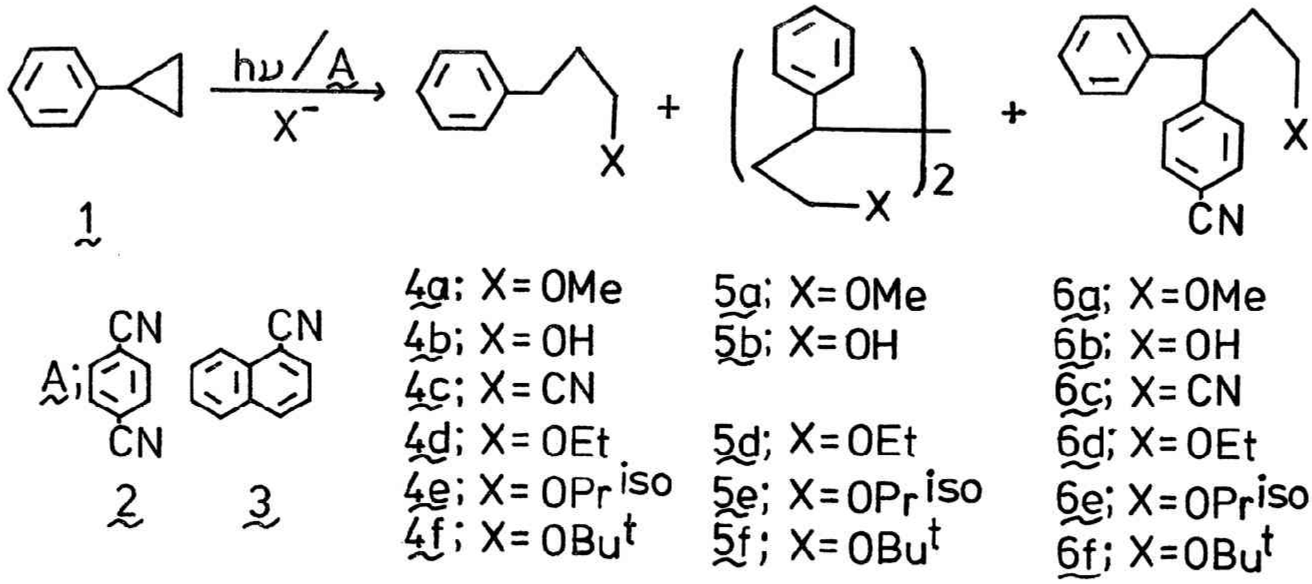
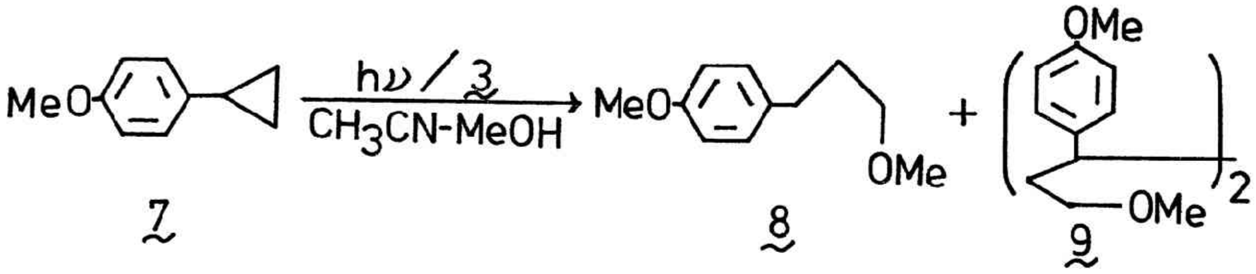
The cyclopropane ring of arylcyclopropanes is oxidatively cleaved by irradiation in polar solvents containing nucleophiles such as alcohols, water, and sodium cyanide in the presence of electron-acceptor such as 1,4-dicyanobenzene and 1-cyanonaphthalene, giving nucleophile-incorporated products. This photoreaction proceeds via an electron-transfer from the cyclopropanes to the excited electron-acceptors, and the cation radicals of arylcyclopropanes are involved as key intermediates.

Photocleavage of the cyclopropane ring in phenylcyclopropane derivatives is a subject of current interest mainly from mechanistic viewpoints.2-4) Recently, Rao and Hixson have reported that phenylcyclopropane undergoes the photochemical addition of methanol accompanied by oxidative cleavage of the cyclopropane ring upon irradiation in the presence of organic electron-acceptor.5) We have also studied independently this sort of photoreactions.6) In this communication, we report our results on the polar addition of various nucleophiles to arylcyclopropanes through a photoinduced electron-transfer and on the reactivity feature of cation radicals produced as intermediates.

Irradiation of an acetonitrile-methanol(3:1) solution containing phenylcyclopropane(1; E^{ox} = 1.38 V)7) (16 mmol) and 1,4-dicyanobenzene(2)(6 mmol) with a high-pressure mercury arc through Pyrex for 30 h gave 4a(17%), 5a(meso- and dl-isomers4); 33%), and 6a(10%).8,9) Similar irradiation of 1 in the presence of 1-cyanonaphthalene(3) afforded 4a(40%) and 5a(45%). Irradiation of p-methoxyphenylcyclopropane(7; E^{ox} = 1.02 V)7) in the presence of 3 gave 8 and 9 as major products. These products were isolated by column chromatography on silica gel, and their structures were assigned from their analytical and spectral properties. On the other hand, no photocleavage occurred upon





irradiation of n-hexylcyclopropane(10; $E^{ox} > 2.0$ V)$^{7)}$ and bicyclo[4.1.0]heptane(11; $E^{ox} = 1.83$ V),$^{7)}$ which have more positive oxidation potentials than those of 1 and 7, in the presence of electron acceptors such as 2 and 3 in acetonitrile-methanol(3:1).

The photocleavage of 1 in the presence of other nucleophiles was also examined. Irradiation of an acetonitrile-water(3:1) solution containing 1 and 2 gave 4b(28%), 5b(9%), and 6b(8%). When a large excess of sodium cyanide was added to the above solution, 4c(8%), 6c(5%, mp 80-81 °C), and 12 were obtained along with small amount of 4b. Similar irradiations of acetonitrile-ethanol, -isopropanol, and -t-butanol(3:1) solutions containing 1 and 2 afforded the corresponding cleaved products, 4d-f, 5d-f, and 6d-f in moderate yields.

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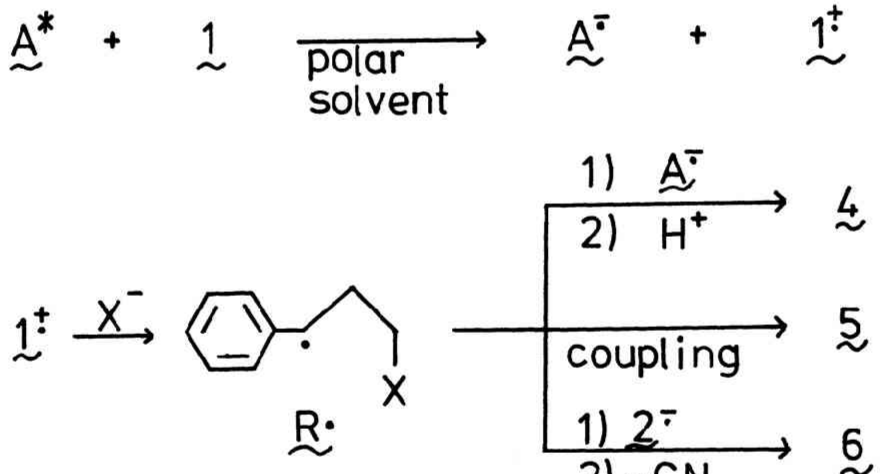
No photocleavage of 1 and 7 occurred in the absence of electron-acceptor 2 or 3. The photoreaction was not observed also upon irradiation in aprotic solvents such as acetonitrile and benzene even in the presence of the electron-acceptor. Thus, it is concluded that both electron-acceptor and nucleophile are essential for the photoinduced cleavage of 1 and 7.

Fluorescence of 3 was efficiently quenched by 1 and 7 in polar solvents such as acetonitrile and methanol in a near diffusion-limiting rate,[10] but less efficiently by 10 and 11. Moreover, negative ΔG values were estimated from Weller's equation for the electron-transfer from 1 and 7 to the photoexcited singlet states of 2 and 3, but positive values were estimated for 10-3 and 11-3 pairs.[11]

The above photoinduced anti-Markownikoff additions of nucleophiles to arylcyclopropanes can be explained in terms of the mechanism shown in Scheme 1. Photoexcitaion of an electron-acceptor(A) such as 2 or 3 in the presence of 1 leads to the formation of the cation radical $1^{+\bullet}$ and the anion radical $A^{-\bullet}$. Nucleophilic attack of methanol or other nucleophiles(X^-) on $1^{+\bullet}$ gives the radical R•. The back electron-transfer from $A^{-\bullet}$ to R• and subsequent protonation afford 4. The coupling of R• gives 5(meso- and dl-isomers). The adducts 6 are formed by the coupling of R• and $A^{-\bullet}$($2^{-\bullet}$; the anion radical of 2), followed by elimination of cyanide ion. This mechanism is further supported from the result that irradiation of 1 and 3 in acetonitrile-CH_3OD (3:1) gave $4a\text{-}d_1$ (d_1 content; 80%) in good yield.[12]



Scheme 1

REFERENCES AND NOTES

1) Supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education(No. 505596).

2) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, J. Am. Chem. Soc., 88, 5675(1966).

3) S. S. Hixson, J. Am. Chem. Soc., 96, 4866(1974); S. S. Hixson and D. W. Garrett, ibid., p. 4872.

4) K. Mizuno, J. Ogawa, H. Kagano, and Y. Otsuji, Chem. Lett., 1981, 437.

5) V. R. Rao and S. S. Hixson, J. Am. Chem. Soc., 101, 6458(1979).

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7) The oxidation potentials of cyclopropanes(**1**, **7**, **10**, and **11**) were measured by cyclic voltammetry; Pt electrode, tetraethylammonium perchlorate(0.1 M) in acetonitrile solution, vs. Ag/0.01 M Ag^+.

8) The UV spectral examination showed that **1** and **2** do not form charge-transfer complex in their ground state.

9) The photoisomerization of polyarylcyclopropanes to polyaryl-substituted propenes via cyclopropane cation radicals have been reported; D. R. Arnold and R. W. R. Humphreys, J. Am. Chem. Soc., 101, 2743(1979); K. Mizuno, H. Kagano, and Y. Otsuji, unpublished results; see also ref. 5. However, irradiation of **1** and **2** in polar solvent did not give the isomerized products such as 1-phenyl-1-propene and 3-phenyl-1-propene in appreciable amounts.

10) Fluorescence of **3** is also quenched by **1** and **7** in cyclohexane. In the case of **7**, a weak exciplex emission(λ_{max} ~ 390 nm) was observed with appearance of an isoemissive point at 370 nm.

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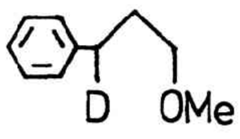

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