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Photoreaction of 2-Aryl-4-methylpent-2-enenitrile Giving 1-Aryl-1-cyano-2,2-dimethylcyclopropane. The Substituent Effect of 1,2-Hydrogen Migration

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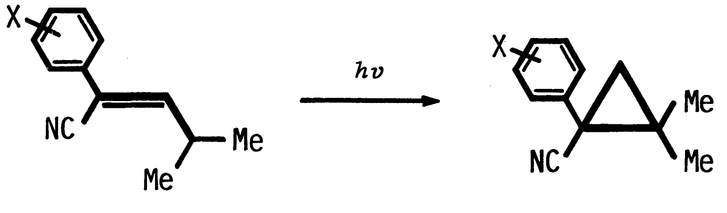
The photorearrangement of 2-aryl-4-methylpent-2-enenitriles to arylcyclopropanes is discussed on the basis of substituent effect. The efficiency of 1,2-hydrogen migration is independent from an electronic effect of the substituent and correlated to the singlet energy of excited molecule.

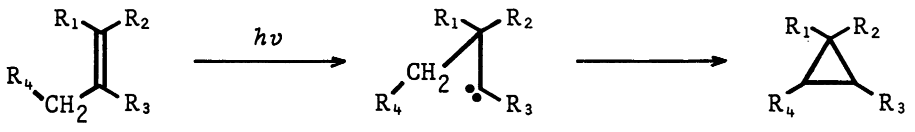
In previous report, we described the photochemical transformation of 2-phenyl-4-methylpent-2-enenitrile (1) leading to 1-cyano-1-phenyl-2,2-dimethylcyclopropane (2).[1] In order to clarify the reaction mechanism of this facile cyclopropane ring formation, several derivatives (1a-e) were synthesized, and the photochemical reactions were investigated in detail on the basis of the chemical and quantum yields in both non polar and polar media.



1 (X= H) 2 (X= H)

1a, 2a: X= p-MeO
1b, 2b: X= m-MeO
1c, 1c: X= p-Me
1d, 2d: X= p-Cl
1e, 2e: X= p-CN

In the photoreaction of simple olefins such as cyclohexene (3) and 2,3-dimethyl-2-butene (4), the generation of cyclopropane (6) has been elucidated by the C-H insertion of carbenes (5) which originate from the 1,2-alkyl migration of Rydberg states.[2] On the other hand, the corresponding aryl olefins (R_2,R_3= Ph) do not give cyclopropanes because of the π-π^* character of the lowest excited states.[3] Only a few derivatives of phenyl-substituted olefins, upon irradiation, give cyclopropanes even in poor yields,[4] and then the photochemical 1,2-hydrogen migration of 1 is noteworthy in connection with the chemical property of excited olefins.



3: R_1—R_4= $(CH_2)_3$, R_2= R_3= H
4: R_1= R_2= R_3= Me , R_4= H

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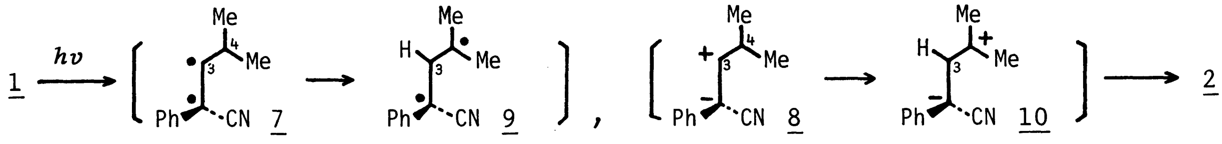
The photoreaction of 1 shows three characteristic points: 1) The π-π^* singlet excited state is responsible for this rearrangement. 2) The structure of photoproduct 2 indicates the 1,2-transfer of C_4-hydrogen to the C_3-position. 3) The reaction yield is extraordinarily high in the presence of nitrile moiety. Thus, the initial active species for photorearrangement is considered to be a nonplanar radicaloid 7 or a charge-separated species 8. The formation of cyclopropane 2 might be explained by a hydrogen migration of 7 and a hydride shift of 8 giving 1,3-diradical 9 and ionic intermediate 10, respectively. Although the dipolar species are plausible intermediates because of the remarkable cyano effect, the radical mechanism is also attractive since one of radical centers would be stabilized by a captodative pair, cyano and phenyl groups.[5] This captodative stabilization is expected to give stable diradicals in which the cyclopropane ring formation might be accelerated. Our original purpose of this research is the control of photoreaction using the enhanced captodative effect, i.e., the introduction of electron-donating group on C_2-phenyl is expected to improve the chemical yield and the reaction efficiency. Otherwise, the electron-withdrawing group might accelerate the hydride-type shift of 8 in accord with the ionic mechanism.

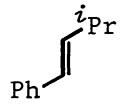


When the synthesized 2-aryl-4-methylpent-2-enenitriles (1a-e)[6] were irradiated in a hexane solution (0.01 mol dm^{-3}) for 3 h using RUL-2537Å lamps (90 W), the 1-aryl-1-cyanocyclopropanes (2a-e)[7] were produced in 80-90% yields. The quantum yields in cyclohexane and acetonitrile are listed in Table 1 along with Hammett's σ-constants.[8]

Table 1. Photoreactions of 1a-e in cyclohexane and acetonitrile (254 nm light)

Compounds	Yields / % (Hexane)	Quantum yields for 2a-e (Cyclohexane)	(Acetonitrile)	Hammett's σ-constants
1a (p-MeO)	90	0.20	0.13	-0.27
1c (p-Me)	80	0.18	0.19	-0.17
1	84	0.26	0.20	0.00
1b (m-MeO)	87	0.10	0.065	0.12
1d (p-Cl)	81	0.20	0.16	0.23
1e (p-CN)	85	0.17	0.11	0.66

The quantum yields for the transformation of 1a-e to 2a-e are not related to the Hammett's parameters and exhibit significantly higher values compared with those of the related compounds, 1-phenyl-3-methyl-1-butene 11 (0.014)[9] and 1,1-diphenyl-3-methyl-1-butene 12 (0.016).[10] This cyano effect distinguished can be rationalized by a stabilization of both diradical and polar species, 7-10.



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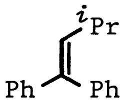

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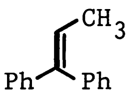

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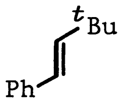

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It is noticeable that the substituent effect observed here is in marked contrast to those of 1,1-diarylpropenes, i.e., 1,1-diphenylpropene (13), $\Phi = 0.00038$; 1,1-bis(4-methoxyphenyl)propene (13a), $\Phi < 0.00005$; 1,1-bis(4-cyanophenyl)propene (13b), $\Phi = 0.0022$.[11] In the case of 1a-e, the electron deficient nature at the migration terminus never promotes the 1,2-migration as shown in the photoreactions of 13 and β-t-butylstyrene (14).[12] The highest value of quantum yields was obtained with the parent compound 1 in a cyclohexane solution. The electron-donating group results in a suppression of cyclopropane formation and the electron-withdrawing group also decreases the efficiencies. In addition, the quantum yields moderately decrease in an acetonitrile solution indicating no polar effect for the 1,2-migration. This tendency eliminates the ionic intermediates as well as the captodative stabilization. Herein the photoreaction of 1 is considered to be a radical process controlled by the initial hydrogen migration in which the reaction efficiency is influenced by the magnitude of singlet energy. The highest E_S of 1, 97.8 kcal/mol, is responsible for the highest efficiency 0.26, and the decrease of E_S, which is induced by both electron donating and withdrawing substituents, results in a significant suppress of reaction efficiency. As a result, the singlet energies (1a: 97.0, 1b: 94.2, 1c: 96.5, 1d: 96.7, and 1e: 95.5 kcal/mol) correlate to the quantum yields with a good linearity shown in Fig. 1.[15] In the photoreactions of 1a-e, the bond dissociation energy of C_4-H is estimated to be 81 kcal/mol,[16] and the C_4-hydrogen of twisted molecule 7 would move to the migration terminus (C_3) by a consumption of excitation energy.

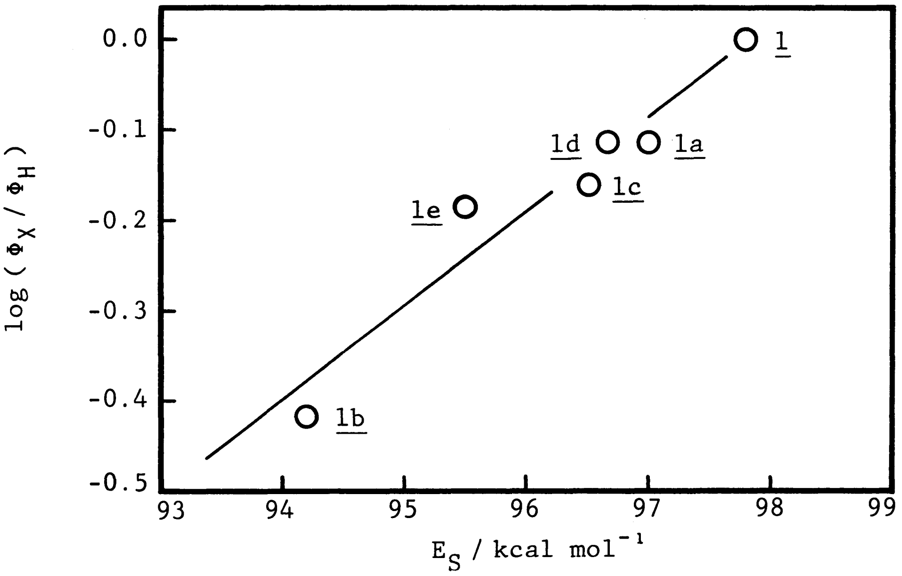

Fig. 1. Quantum yields (Φ) *vs.* singlet energy (E_S).

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3) For example, the corresponding cyclopropanes could not be obtained by the photolysis of α-, β-methylstyrene, and 1-phenylcyclohexene.

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5) H.G. Viehe, Z. Janousek, R, Merenyi, and L. Stella, Acc. Chem. Res., 18, 148 (1985).

6) Compound 1a, bp 69-71 °C (0.04 mm), λmax= 274.1 (ε 14530) nm in cyclohexane; 1b, bp 78-80 °C (0.03 mm), 238.7 (13620), 261.9 (8130), 298.1 (2830) nm; 1c, bp 66-67 °C (0.04 mm), 264.1 (13170) nm; 1d, mp 56-58 °C, 263.6 (14670) nm; 1e, mp 102-103 °C, 267.6 (20140) nm.

7) Product 2a, bp 89-92 °C (0.04 mm); 2b, bp 87-90 °C (0.05 mm); 2c, bp 89-91 °C (0.04 mm); 2d, mp 62.5-63.5 °C; 2e, mp 92-93 °C.

8) The quantum yields were measured with 254 nm light by potassium ferrioxalate actinometry.

9) S.S. Hixson, J. Am. Chem. Soc., 98, 1271 (1976)

10) The irradiation of 1,1-diphenyl-3-methyl-1-butene 12 gave 1,1-dimethyl-2,2-diphenylcyclopropane in 76% yield. The quantum yield was determined to be 0.016 which was slightly different from the value 0.012 reported by Hixson.11)

11) S.S. Hixson, J. Chem. Soc., Chem. Commun., 1975, 515.

12) The analogous effect was observed in the photoreaction of -t-butylstyrene (14) where the 1,2-methyl migration of the p-cyano derivative (14b) was faster than that of 14 by a factor of three.13) In addition, the irradiations of 14 and the p-methoxy derivative (14a) gave the methanol-adducts indicating the polarization in reverse.14) We did not consider the corresponding polar species in the photoreactions because of no detectable methanol-adduct in any case.

13) S.S. Hixson and T.P. Cutler, J. Am. Chem. Soc., 95, 3032 (1973).

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15) The singlet energies were determined from the 0-0 bands in the electronic spectra in methylcyclohexane at 77 K. This substituent effect should be discussed on the basis of the reaction rates as well as the quantum yields. In this stage, the consideration is limited in a relation between singlet excitation energy and quantum yield, since no fluorescence was observed in these compounds at all. It is known that the quantum yields for the p-methoxy and p-cyano derivatives (14a and 14b) of β-t-butylstyrene are correlated to the reaction rates of the photochemical 1,2-methyl migrations.13)

16) This value was calculated for a model compound, 3-methylbutene, in accord with the procedure of Kerr. J.A. Kerr, Chem. Rev., 66, 465 (1966).

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