Tetrahedron Letters,Vol.27,No.51,pp 6225-6228,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

PHOTOREACTION OF α-PHENYLCROTONONITRILE DERIVATIVES: THE FACILE CYCLOPROPANE RING FORMATION[1]

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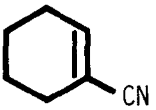
Summary: Irradiation of 4-methyl, 4,4-dimethyl, and 4,4,4-trimethyl derivatives of 2-phenylcrotononitrile gives the corresponding 1-cyano-1-phenylcyclopropanes in high yields.

Photoreaction of olefins leading to the formation of cyclopropane ring have been attractive for the synthetic utility. This procedure have difficulty in practical cases because of the contaminative side reactions.[2] Recently, McCullough reported the selective formation of cyclopropane ring by the photolysis of cyano-substituted olefins, 1 and 2.[3] This photoreaction induced by the cyano-substitution is of interest in both synthetic and mechanistic viewpoints. In order to gain an insight into the structure-photoreactivity relationship of cyano-substituted olefins, our research was extended to acyclic system, crotononitrile (3) and its α-phenyl derivatives (4a-d). In this paper, we wish to describe the extraordinarily facile photorearrangement of 4 producing cyclopropanes.



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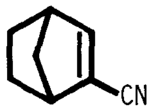

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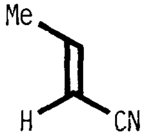

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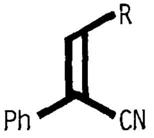
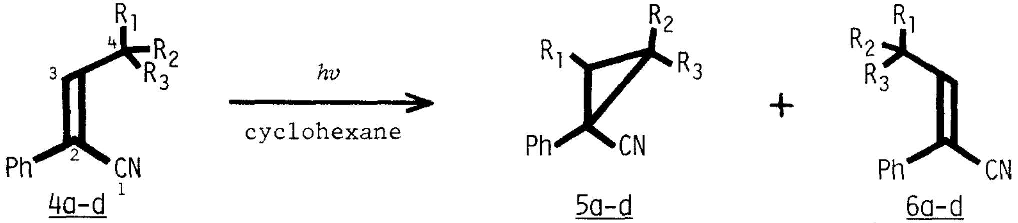


4

R = Me
Et
i-Pr
t-Bu

The direct irradiation of crotononitrile (3) using RUL-2537Å lamps induced only a cis-trans isomerization between E- and Z-isomer but no cyanocyclopropane expected could be detected in the photolysis mixture. On the other hand, 2-phenylcrotononitrile (4a)[4] afforded 1-cyano-1-phenylcyclopropane (5a)[5] in 14 % yield. Furthermore, the methyl substitutions at the C_4 position resulted in a significant improvement of the cyclopropane formation process, i.e., the irradiation of the 4-methyl, 4,4-dimethyl, and 4,4,4-trimethyl derivatives (4b-d)[4] afforded 1-cyano-1-phenylcyclopropanes (5b-d)[7] in 80, 88, and 83 % yield, respectively. The photolysis conditions, reaction and quantum yields are shown in Table 1. In these photoreactions, the formation of E-isomers 6a-d[8] was a major photochemical process in the initial stage and the prolonged irradiations gave the corresponding cyclopropanes 5a-d which were isolated by column chromatography on silica gel.[9]

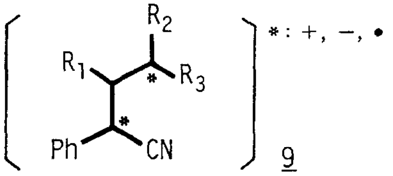


(a : $R_1 = R_2 = R_3 = H$ b : $R_1 = R_2 = H$, $R_3 = Me$
c : $R_1 = H$, $R_2 = R_3 = Me$ d : $R_1 = R_2 = R_3 = Me$)

Table 1. Photoreactions of 4a-d in cyclohexane (2.0 x10^{-2}M, RUL-2537Å 105 W).

Reactant	Irradiation Time (min)	Reaction Yields (%) 4	5	6	Quantum Yields 4 to 5	4 to 6
4a	30	52	3	43	0.01	0.42
	120	30	14	42		
4b	30	51	13	36	0.09	0.36
	200	4	80	5		
4c	30	41	24	35	0.26	0.29
	120	2	88	4		
4d	30	39	8	53	0.039	0.48
	300	2	83	13		

The formation of cyclopropanes 5a-d is induced from the π-π^* singlet excited state of the cyano-substituted olefins 4a-d. The most remarkable result is the high yields and efficiencies which are hitherto unknown in the photoreaction of olefins producing cyclopropane ring. For example, the quantum yield of β-t-butylstyrene (7)[10] and 1,3-diphenylpropene (8)[11] leading to cyclopropanes was only 0.001 and 0.005, respectively.



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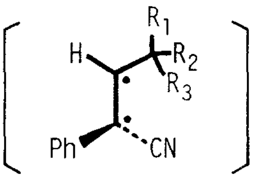


10

The structure of photoproducts indicates that the 1,2-hydrogen (methyl) migration occurs on the excited state to produce intermediates 9. Although the ionic intermediate is an attractive one,[12] there is no evidence in this stage. In fact, the irradiations in acetonitrile or methanol did not give remarkable solvent effect. Here, the most plausible intermediate is considered to be a 1,3-diradical originated from the 1,2-radical migration. The intermediate 9 should be a long lived radical since both Z- and E-isomer gave the same epimer ratio (5:4 and 25:1) in the photoreactions of the ethyl and t-butyl derivatives[7]. Two active species are considered as a precursor of 1,3-diradical 9. The first candidate, a twisted excited molecule 10, which is responsible for cis-trans isomerization, seems not to be suitable for the precursor leading to cyclopropane because of the facile decay process to ground state. Another active species is the Franck-Condon excited state of olefins, i.e., the excited molecule keeping the ground state geometry initiates the 1,2-migration to give 1,3-diradical intermediates 9a-d which are stabilized by both phenyl and cyano group.

A facile cyclopropane formation observed in the photolysis of 4b-d is mainly ascribed to the stabilizations of radical intermediate by the methyl, phenyl, and cyano groups. The lower efficiency with 4d compared with 4c is attributed to the mass of migration group. In addition, the configuration of excited state would be important in order to understand this unique photochemical 1,2-migration. Inspection of the electronic spectra, the π-π^* absorptions of 4a-d exhibit the absorption maxima at 255-257 nm and these absorptions are entirely similar to those of styrene derivatives except for the bathochromic shift of 10 nm. The E-isomers 6a-d show a marked blue shift of π-π^* absorption[8] but the irradiations of 6c and 6d under similar condition afforded cyclopropanes 5c and 5d in high yields, 84 and 93 %. The lack of co-planarity in styrene chromophore, which is induced by the steric repulsion between the 2-phenyl and the 4-methyl group, is convenient for the cyclopropane formation. In fact, the quantum yields show higher values, $\Phi = 0.28$ (6c to 5c) and 0.093 (6d to 5d) in comparison with those of 4c and 4d. The difference of reaction

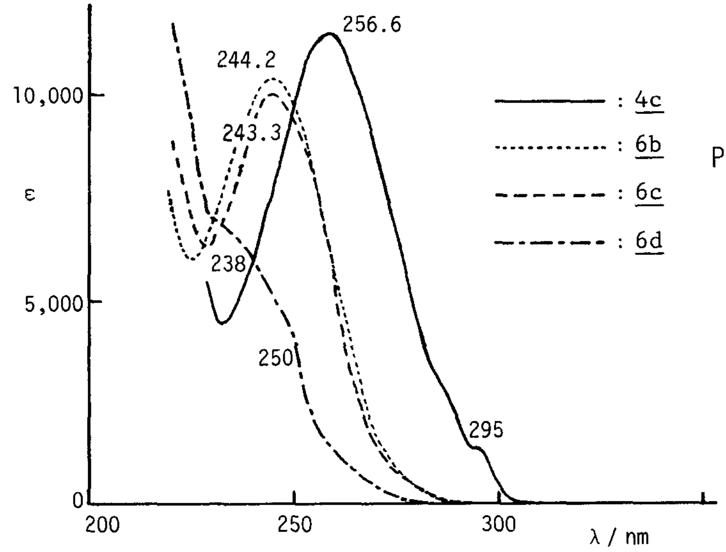
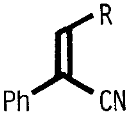
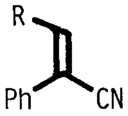


Fig. 1 Electronic Spectra of 4c and 6b-d

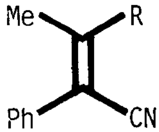


4a-d ,



6a-d

R = Me, Et, i-Pr, t-Bu



11a-c

R = Me
Et
i-Pr

efficiency between Z- and E-isomer also excludes the contribution of the twisted intermediate 10 for cyclopropane ring formation. In addition, this kind of 1,2-migration reaction could not occur on the irradiations of the 3-methyl derivatives 11a-c[13] indicating that the bulkiness of C_3 substituent suppresses the migration reaction from C_4-carbon to C_3-carbon.

The photoreaction of α-phenylcrotononitriles was uncovered to give valuable informations to the chemical behavior of excited olefins as well as the remarkable facility for cyclopropane formation. Further study for the photochemistry of cyano-olefins is in progress.

References and Notes

1. Organic Photochemistry 78. Part 77: T. Miyashi, M. Kamata, and T. Mukai, J. Am. Chem. Soc., in press.
2. S.S. Hixson, J. Am. Chem. Soc., 98, 1271 (1976).
3. I.A. Akhtar, J.J. McCullough, S. Vaitekunas, R. Faggiani, and C.J.L. Lock, Can. J. Chem., 60, 1657 (1982); J.J. McCullough and C. Manning, J. Org. Chem., 43, 2839 (1978).
4. Compound 4a,[5] λmax= 255.1 (ε 10550) nm; 4b,[6] 256.0 (11180) nm; 4c,[6] 256.6 (11460) nm; 4d, bp 62-64°C/0.06mmHg, 255.9 (10730) nm in cyclohexane.
5. E.C. Knowles and J.B. Cloke, J. Am. Chem. Soc., 54, 2028 (1932).
6. J.V. Murray and J.B. Cloke, J. Am. Chem. Soc., 58, 2014 (1936).
7. Product 5b, a 5:4 mixture of two epimers; the major cis-isomer, 2240 cm^{-1}, 1.2-1.7(6H, m), 7.30(Ph); the trans-isomer, 2235 cm^{-1}, 0.81(3H, d, 3.0 Hz), 1.2-1.35(1H, m), 1.6-2.0(2H, m), 7.37(Ph); 5c, mp 48-49°C, 2240 cm^{-1}, 0.80 (3H, s), 1.32(1H, d, 2.2 Hz), 1.45(1H, d, 2.2 Hz), 1.51(3H, s), 7.1-7.4 (Ph); 5d, a 25:1 mixture of two epimers; the major cis-isomer, bp 64-66°C/ 0.08mmHg, 2225 cm^{-1}, 0.80(3H, s), 1.37(3H, s), 1.3-1.8(4H, m), 7.21(Ph); the trans-isomer, 2225 cm^{-1}, 0.94(3H, s), 1.01(3H, d, 7.0 Hz), 1.42(1H, q, 7.0 Hz), 1.52(3H, s), 7.27(Ph).
8. Product 6a, λmax= 243.2 (ε 10820) nm ; 6b, 244.2 (10470) nm ; 6c, 243.3 (10020) nm ; 6d, 238 (sh, 6140) nm in cyclohexane.
9. The 1,3-hydrogen migration products, 2-phenylpent-3-enenitriles and 2-phenyl-4-methylpent-3-enenitrile, were obtained as the side products in 1-4 % yields which were separated on the column chromatography.
10. S.S. Hixson and T.P. Cutler, J. Am. Chem. Soc., 95, 3032 (1973).
11. S.S. Hixson, J. Am. Chem. Soc., 94, 2507 (1972).
12. In ground state chemistry, 1,2-radical migration is unfamiliar. When the migration to cationic center is considered in this case, the cyano-substitution at C_2-position seems to stabilize the intermediate 9.
13. 3-Methyl-2-phenylbutenonitrile, 3-methyl-2-phenylpentenonitrile, and 3,4-dimethyl-2-phenylpentenonitrile (11a-c) were synthesized and irradiated under similar conditions.

(Received in Japan 7 August 1986)