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9,10-Dicyanoanthracene-Sensitized NO Insertion into Cyclopropane Ring via Photoinduced Electron Transfer

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9,10-Dicyanoanthracene-sensitized photoreaction of electron-rich 1,2-diarylcyclopropanes with NO in acetonitrile afforded 3,5-diaryl-2-isoxazolines in good yields. The cyclopropanes bearing different aryl-substituents gave a mixture of two isomeric 2-isoxazolines. Mechanistic features of this reaction are described.

Photooxygenation of small ring compounds via electron transfer is an active research area in recent years.[1)] However, there is no report about NO insertion into these compounds. We now describe the first example of the NO insertion into cyclopropane ring using NO gas via photoinduced electron transfer.

Nitrogen was bubbled into an acetonitrile solution containing 1,2-bis(4-methoxyphenyl)cyclopropane (**1a**) (0.01 mol dm^{-3}) and a catalytic amount of 9,10-dicyanoanthracene (DCA, 1×10^{-4} mol dm^{-3}) for more than 15 min, and then NO stream was blown through for 5 min. Irradiation of the mixture with >400 nm light for 3 h gave 3,5-bis(4-methoxyphenyl)-2-isoxazoline (**2a**) in a 91% isolated yield.

Similar irradiation of **1b** and **1e-f** gave the corresponding 3,5-diaryl-2-isoxazolines (**2b** and **2e-f**). When unsymmetrically substituted 1,2-diarylcyclopropanes **1c-d** were used as substrates, positional isomeric mixtures **2c-d** and **3c-d** were obtained. However, electron-poor cyclopropane **1g** did not give the 2-isoxazoline. The results are summarized in Table 1. The NO insertion products were isolated by column chromatography on silica gel. The structures of the products were determined by comparison of their spectral (^1H NMR, IR, MS) properties with these of the compounds previously obtained.[2)]

The fluorescence of DCA was efficiently quenched by the cyclopropanes **1a-f** at nearly diffusion controlled rates in acetonitrile and benzene.[1a,3)] However, the photoreaction of **1a** with NO in benzene gave no product. The formation of **2a** was completely quenched by the addition of triethylamine (0.01 mol dm^{-3}). From these results, the electron transfer mechanism shown in Scheme 1 is proposed for the

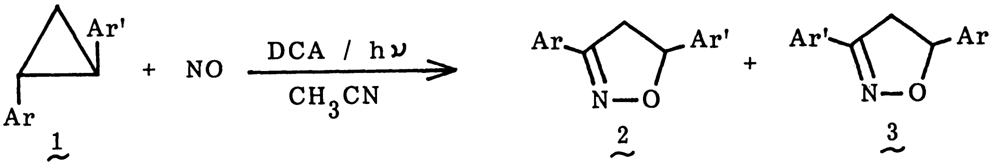
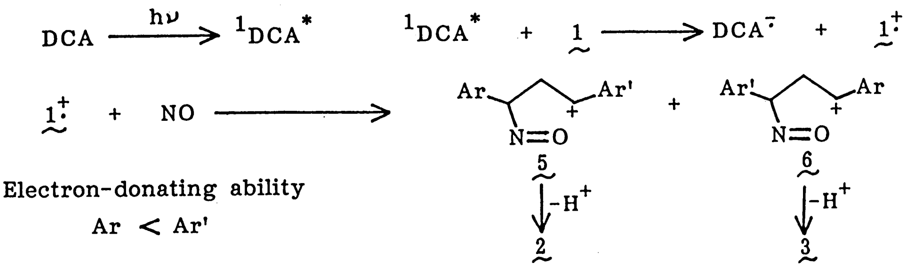


Table 1. DCA-Sensitized Photoinsertion of NO into 1,2-Diarylcyclopropanes

Compd	Ar	Ar'	$E^{ox}_{p/2}/V$ a)	ΔG b) kJ/mol	Time h	Yield c) %	Isomer ratio d) 2 : 3
1a	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	0.55	-103.2	3.0	91	
1b	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	0.90	-69.5	3.0	55	
1c	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3OC_6H_4$	0.82	-77.2	3.0	57	8 : 2
1d	$4\text{-}ClC_6H_4$	$4\text{-}CH_3OC_6H_4$	0.82	-77.2	3.0	34	7 : 3
1e	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	1.06	-54.0	3.0	31	
1f	C_6H_5	C_6H_5	1.14	-46.3	3.0	17	
1g	$4\text{-}CNC_6H_4$	$4\text{-}CNC_6H_4$	1.26	-34.7	3.0	0	

a) Oxidation potentials of cyclopropanes vs. Ag/Ag^+ in acetonitrile. b) The calculated free energy changes for the one-electron transfer process from the cyclopropanes to $^1DCA^*$ in acetonitrile. See Ref. 1a. c) Isolated yields. The total yields of 2c-d and 3c-d are shown for unsymmetrically substituted substrates 1c-d. d) Determined by 270 MHz ^1H NMR.

DCA-sensitized NO insertion reaction. The one-electron transfer from cyclopropane 1 to a singlet excited state of DCA ($^1DCA^*$), affords radical cation $1^{+\cdot}$ and radical anion $DCA^{-\cdot}$.[4] This process is exothermic. The radical cation $1^{+\cdot}$ reacts with NO to give 2 and 3 via the cationic intermediates 5 and 6. The regioselectivity in this reaction may be determined by the stability of these cationic intermediates.



Scheme 1.

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References

1) a) K. Mizuno, N. Kamiyama, N. Ichinose, and Y. Otsuji, Tetrahedron, 41, 2207 (1985); b) A. P. Schaap, S. Siddiqui, G. Prasad, E. Palomino, and M. Sandison, ibid., 41, 2229 (1985); S. Futamura, S. Kusunose, H. Ohta, and Y. Kamiya, J. Chem. Soc., Perkin Trans. 1, 1984, 15; T. Miyashi, M. Kamata, and T. Mukai, J. Am. Chem. Soc., 109, 2780 (1987) and references cited therein.

2) The reaction of 1a-f with $NOBF_4$ gave 3,5-diaryl-2-isoxazolines 2a-f in good yields: N. Ichinose, K. Mizuno, T. Tamai, and Y. Otsuji, Chem. Lett., 1988, 233.

3) Fluorescence of DCA was also quenched by NO.

4) Most of DCA was recovered.

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