

Novel Photoreactions of Styrylcyclopropanes via Photo-induced Electron Transfer

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9,10-Dicyanoanthracene-sensitized photoreaction of styrylcyclopropanes in the presence of $\text{Cu}(\text{BF}_4)_2$ in MeCN–MeOH gives α -cyclopropyl benzyl ketones as major products, which are produced via a two-electron oxidation of styrylcyclopropanes followed by a 1,2-migration of the cyclopropyl group.

Recently, much attention has been focused on the reactivity of cation radicals of organic substrates generated by a photo-induced electron transfer.^{1–3} We have recently reported the 1,2- and 1,3-dialkoxylations of aromatic olefins and cyclopropanes using the 9,10-dicyanoanthracene (DCA)–copper(II) sensitizer system.⁴ We now report a novel photoreaction of the styrylcyclopropanes (**1a**) and (**1b**) using this sensitizer system, involving a two-electron oxidation and a 1,2-migration of the cyclopropyl group.

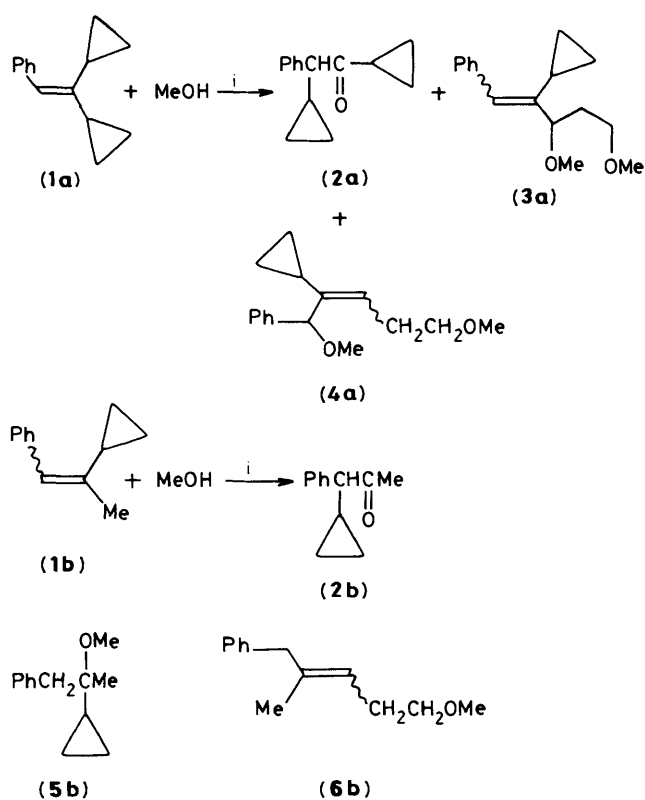
Irradiation of a MeCN–MeOH (2:1) solution of (**1a**) (3 mmol) in the presence of DCA (0.003 mmol) and $\text{Cu}(\text{BF}_4)_2$ (7 mmol) through an aqueous CuSO_4 – NH_3 filter solution (405 nm light) with a 500 W high-pressure mercury arc for 10 h gave compounds (**2a**), (**3a**), and (**4a**) in 53, 13, and 8% isolated yields, respectively. Similar irradiation of (**1b**) (as a mixture of *cis*- and *trans*-isomers) gave (**2b**) as the major isolable product

in 57% yield.[†] The products were isolated by column chromatography on silica gel and preparative g.l.c. and the structures were assigned from their spectral (¹H n.m.r., i.r., u.v., and mass) properties and elemental analyses.[‡]

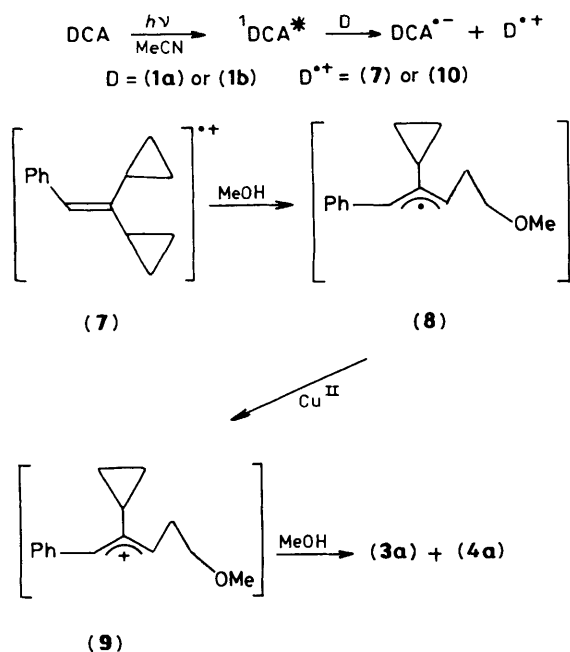
The fluorescence of DCA was efficiently quenched by (**1a**) and (**1b**) at a nearly diffusion-controlled rate [$k_q = 1.34 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for (**1a**) and $1.10 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for (**1b**)] and the free energy changes [$\Delta G = -99.5 \text{ kJ mol}^{-1}$ for (**1a**)

[†] The u.v. spectra showed that charge-transfer complexes of (**1a**) and (**1b**) with DCA are not formed in the ground states.

[‡] E.g. for compound (**2a**): oil, i.r. ν_{max} (neat) 1690 cm^{-1} ; ¹H n.m.r. $\delta(\text{CCl}_4)$ 0.1–0.6 (4H, m, CH_2), 0.6–1.0 (4H, m, CH_2), 1.1–1.4 (1H, m, CH), 1.55–1.85 (1H, m, CH), 2.95 (1H, d, J 9.0 Hz, CH), and 7.1 (5H, s, ArH); m/z 200 (M^+), 131, 91, 77, 69, and 41.

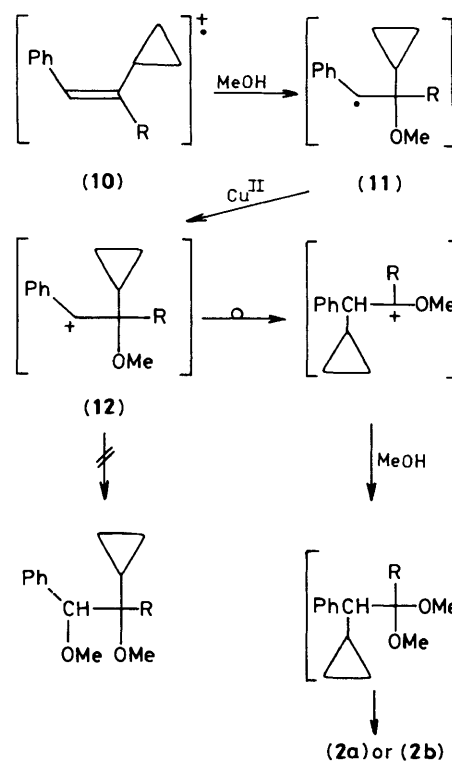


i, hv, DCA-Cu^{II}, MeCN



Scheme 1

and $-95.7 \text{ kJ mol}^{-1}$ for (1b)], estimated by the Rehm-Weller equation, for one-electron transfer from (1a) and (1b) to the excited singlet DCA (¹DCA*) were negative.⁵ The photoreaction of (1a) and (1b) did not occur in the absence of DCA and/or Cu(BF₄)₂, nor in aprotic solvents.



Scheme 2. R = cyclopropyl or Me.

These results suggest that the photoreaction proceeds via the mechanism shown in Schemes 1 and 2. The formation of (3a) and (4a) can be explained by an anti-Markovnikov attack of methanol on the cyclopropane ring of the cationic radical (7),^{4,6,7} which is generated by electron transfer from (1a) to ¹DCA*, followed by the oxidation of the allyl radical (8) with Cu^{II} ion and nucleophilic attack of methanol on (9) (Scheme 1).

The formation of compounds (2a) and (2b) involves a cyclopropyl group migration (Scheme 2). In this case, the olefinic part of the cationic radical (10) is attacked by methanol in an anti-Markovnikov manner. The other feature of this reaction is that in cation (12) a 1,2-migration of the cyclopropyl group occurs at much faster rate than methyl migration and nucleophilic attack of methanol on (12).⁸

This mechanism was supported by the following observations. (i) The product (2b) was also obtained in 52% yield on irradiation of (1b) in MeCN-EtOH (2:1) in place of MeCN-MeOH. (ii) In the dark, the dimethyl acetal of (2b) was completely decomposed to (2b) in the presence of Cu(BF₄)₄ in MeCN-MeOH (2:1). (iii) When the photoreaction was carried out under oxygen, benzaldehyde was isolated as the major product.⁹

The direct photoirradiation of vinylcyclopropanes usually gives cyclopentene derivatives.¹⁰⁻¹³ However, a photorearrangement of this type does not occur in the DCA-sensitized photoreaction of (1a) and (1b) even in the absence of Cu^{II} ion. Irradiation of a MeCN-MeOH (2:1) solution of (1b) in the presence of 1,4-dicyanobenzene through Pyrex gave the anti-Markovnikov adduct (5b), in 45% isolated yield.¹⁴ It is noteworthy that the acid-catalysed hydrolysis of (1b) in MeOH in the dark gave the homoallyl methyl ether (6b).¹⁵

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References

- 1 M. Julliard and M. Chanon, *Chem. Rev.*, 1983, **83**, 425.
 - 2 R. S. Davidson, *Adv. Phys. Org. Chem.*, 1983, **19**, 1.
 - 3 S. L. Mattes and S. Farid, *Org. Photochem.*, 1983, **6**, 233.
 - 4 K. Mizuno, K. Yoshioka, and Y. Otsuji, *Chem. Lett.*, 1983, 941.
 - 5 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.
 - 6 V. R. Rao and S. S. Hixson, *J. Am. Chem. Soc.*, 1979, **101**, 6458.
 - 7 K. Mizuno, J. Ogawa, and Y. Otsuji, *Chem. Lett.*, 1981, 741.
 - 8 Y. E. Rhodes and T. Takino, *J. Am. Chem. Soc.*, 1970, **92**, 5270.
 - 9 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083.
 - 10 H. Kristinsson and G. S. Hammond, *J. Am. Chem. Soc.*, 1967, **89**, 5970.
 - 11 M. J. Jorgenson, *J. Am. Chem. Soc.*, 1969, **91**, 6432.
 - 12 P. H. Mazzocchi and R. C. Ladenson, *Chem. Commun.*, 1970, 469.
 - 13 S. S. Hixson, *Org. Photochem.* 1979, **4**, 191.
 - 14 A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Am. Chem. Soc.*, 1978, **100**, 538.
 - 15 M. Julia, S. Julia, and S. Y. Tchen, *Bull. Soc. Chim. Fr.*, 1961, 1849.
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