## Novel Photoreactions of Styrylcyclopropanes via Photo-induced Electron Transfer

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9,10-Dicyanoanthracene-sensitized photoreaction of styrylcyclopropanes in the presence of Cu(BF<sub>4</sub>)<sub>2</sub> in MeCN–MeOH gives  $\alpha$ -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 photoinduced electron transfer.<sup>1–3</sup> 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.<sup>4</sup> We now report a novel photoreaction of the styrylcyclopropanes (**1a**) and (**1b**) using this sensitizer system, involving a two-electron oxidation and a 1,2migration 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  $Cu(BF_{4})_2$  (7 mmol) through an aqueous  $CuSO_4$ –NH<sub>3</sub> 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.<sup>†</sup> The products were isolated by column chromatography on silica gel and preparative g.l.c. and the structures were assigned from their spectral (<sup>1</sup>H n.m.r., i.r., u.v., and mass) properties and elemental analyses.<sup>‡</sup>

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)

 $\pm E.g.$  for compound (2a): oil, i.r.  $v_{max}$ . (neat) 1690 cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $\delta$ (CCl<sub>4</sub>) 0.1—0.6 (4H, m, CH<sub>2</sub>), 0.6—1.0 (4H, m, CH<sub>2</sub>), 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*<sup>+</sup>), 131, 91, 77, 69, and 41.

<sup>&</sup>lt;sup>+</sup> The u.v. spectra showed that charge-transfer complexes of (1a) and (1b) with DCA are not formed in the ground states.

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i, hv, DCA-Cu<sup>II</sup>, 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 (<sup>1</sup>DCA<sup>\*</sup>) were negative.<sup>5</sup> The photoreaction of (1a) and (1b) did not occur in the absence of DCA and/or Cu(BF<sub>4</sub>)<sub>2</sub>, 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-Markownikov attack of methanol on the cyclopropane ring of the cation radical (7),<sup>4,6,7</sup> which is generated by electron transfer from (**1a**) to <sup>1</sup>DCA<sup>\*</sup>, followed by the oxidation of the allyl radical (8) with Cu<sup>II</sup> 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 cation radical (10) is attacked by methanol in an anti-Markownikov 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).<sup>8</sup>

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(BF)<sub>4</sub> in MeCN–MeOH (2:1). (iii) When the photoreaction was carried out under oxygen, benzaldehyde was isolated as the major product.<sup>9</sup>

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

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