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9,10-DICYANOANTHRACENE-SENSITIZED TWO-ELECTRON OXIDATION OF PHENYLCYCLOPROPANE AND AROMATIC OLEFINS IN THE PRESENCE OF COPPER(II) ION

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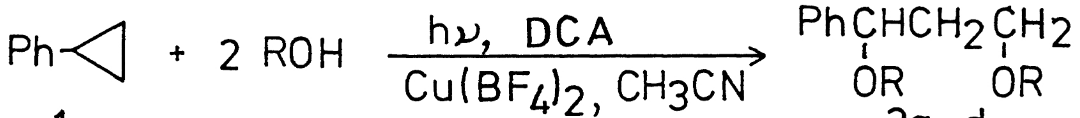
The photooxidation of phenylcyclopropane, styrene, and indene using 9,10-dicyanoanthracene-$Cu(BF_4)_2$ sensitizer system in acetonitrile-alcohol(3:1) solutions affords the corresponding 1,3-dialkoxy and 1,2-dialkoxy compounds.

Recently, much attention has been focussed on the reactivities of cation radicals which are generated via photoinduced electron-transfer from aromatic olefins and arylcyclopropanes.1-8) The cation radicals thus generated are subject to a nucleophilic attack if an appropriate nucleophile is present in the system. Arnold and his coworkers have reported the anti-Markownikoff addition of nucleophiles to aromatic olefin cation radicals.2) Hixson's group3) and we4) have independently reported the anti-Markownikoff-type photoaddition of nucleophiles to arylcyclopropane cation radicals. It is, however, anticipated that these cation radicals or intermediates derived from them would be further oxidized if the photoreaction is carried out in the presence of an appropriate oxidizing agent, and thus new photochemistry may be developed.5) We now report the 9,10-dicyanoanthracene(DCA)-sensitized two-electron oxidation of phenylcyclopropane and aromatic olefins in the presence of copper(II) ions.

Irradiation of an acetonitrile-methanol(3:1) solution containing phenylcyclopropane(**1**, 0.028 mol/dm^3), 0.01 molar equiv of DCA(2.8×10^{-4} mol/dm^3), and 2 molar equiv of copper(II) tetrafluoroborate($Cu(BF_4)_2$, 0.056 mol/dm^3), with a 300W high-pressure mercury arc through an aqueous $CuSO_4$-NH_3 filter solution(405 nm light) for 8 h gave 1,3-dimethoxy-1-phenylpropane(**2a**) in 84% yield, accompanied by the formation of $CuBF_4(CH_3CN)_4$.9-11) The controlled experiments showed that (1) in the absence of DCA and/or $Cu(BF_4)_2$, no product was obtained with a quantitative recovery of **1**, (2) the yield of **2a** decreases with decreasing the amount of $Cu(BF_4)_2$ added, and the most effective sensitizer system for this photoreaction is DCA-$Cu(BF_4)_2$ although other copper(II) ions such as $Cu(ClO_4)_2$, $CuSO_4$, and $Cu(OSO_2CF_3)_2$ and aromatic nitriles such as 1,4-dicyanonaphthalene and 1-cyanonaphthalene are also effective.

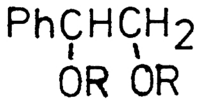


1 **2a-d**

a; R=Me, **b**; R=Et, **c**; R=i-Pr, **d**; R=t-Bu

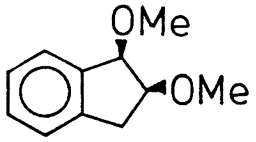
The photoreactions of **1** in the presence of various alcohols under similar conditions afforded the corresponding 1,3-dialkoxy-1-phenylpropanes **2b-d** (Table 1). These products were isolated by distillation or column chromatography on silica gel. The structures were assigned from their analytical and spectral (^{1}H NMR, IR, mass) data.12)

Aromatic olefins such as styrene **3** and indene **5** were converted to the 1,2-dialkoxy compounds **4a-b**, **6c**, and **6t** in good yields by the similar photoreactions using the DCA-Cu$(BF_4)_2$ sensitizer system (Table 1). The photoinduced dialkoxylations of **1**5c) and styrenes5a-b) in the presence of copper(II) ions have previously been reported, but the excitation wavelength for these reactions was limited to shorter wavelength (≤300 nm) and the isolated yields based on the substrates used were relatively low.5)

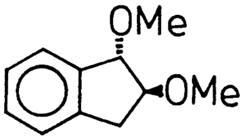


$\mathrm{Ph}\underset{\mathrm{OR}}{\mathrm{CH}}\underset{\mathrm{OR}}{\mathrm{CH_2}}$

4a;R=Me, **4b**;R=Et



6c



6t

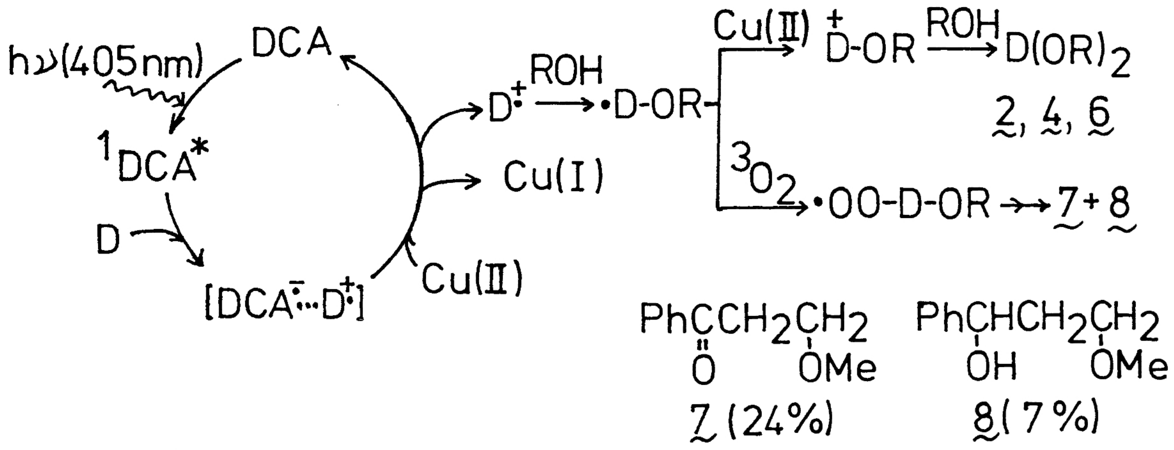
Scheme 1 shows a probable mechanism for the photoreaction reported in this paper. The first step is the photoinduced electron-transfer from an electron-donor molecule (D; **1**, **3**, and **5**) to an excited singlet state of DCA ($^1DCA^*$) to produce the ion radical pair [$DCA^{\bar{\cdot}} \cdots D^{\dot{+}}$]. This electron-transfer would be exothermic process; indeed, the fluorescence of DCA in acetonitrile or methanol was quenched by **1**, **3**, or **5** in near diffusion controlled rate, and the Rehm-Weller equation predicted negative ΔG values for this electron-transfer process.13,14) However, no product was obtained in the absence of Cu(II), suggesting that in this case the [$DCA^{\bar{\cdot}} \cdots D^{\dot{+}}$] is rapidly quenched by a back-electron transfer. Therefore, the Cu(II) ion should play

Table 1. Photooxidation of Phenylcyclopropane, Styrene, and Indene

Substrate	Alcohol	Product	Bp/°C/mmHg	Yield/%a)
1	MeOH	**2a**b)	107-108/15	84
1	EtOH	**2b**	135-137/22	89
1	i-PrOH	**2c**	143-145/23	89
1	t-BuOH	**2d**	153-154/23	89
3	MeOH	**4a**c)	115-116/24	45
3	EtOH	**4b**	124-126/22	41
5	MeOH	**6c** + **6t** (1:1)	134-136/22	90

a) Isolated yields based on the substrates used. The dimeric products such as meso- and dl-1,6-dimethoxy-3,4-diphenylhexanes and meso- and dl-1,4-dimethoxy-2,3-diphenylbutanes were not obtained in this reaction condition; cf. ref. 5a-c. b) Ref. 5c. c) Refs. 5a-b.

Scheme 1



an important role in this photoreaction. Firstly, the Cu(II) ion oxidizes DCA$^{\cdot-}$ to regenerate DCA.15) Consequently, the back-electron transfer from DCA$^{\cdot-}$ to D$^{+\cdot}$ is prevented and the formation of the free D$^{+\cdot}$ is fascilitated. Secondly, the Cu(II) ion oxidizes the radical intermediate •D-OMe,5,16) which is formed by the nucleophilic attack of methanol to D$^{+\cdot}$. The cation intermediate thus produced affords the dimethoxy compounds by the reaction with methanol.

The formation of 2a was efficiently quenched by the addition of 1,4-dimethoxybenzene(DMB)([DMB]=0.05 mol/dm^3) or 1,3,5-trimethoxybenzene(TMB)([TMB]=0.05 mol/dm^3), which has lower oxidation potential than 1.14) Moreover, the addition of oxygen efficiently quenched the formation of 2a; instead oxygenated products 7 and 8 were regioselectively obtained. The oxygenation of the radical •D-OMe to the peroxy radical •OO-D-OMe is expected to be very fast, probably faster than the formation of +D-OMe by Cu(II) ion.7b,17) Decomposition of this peroxy radical or its hydroperoxide by Cu(II) ion gives 7 and 8. No hydroperoxide was detected under the reaction conditions.

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9) $CuBF_4(CH_3CN)_4$ complex was isolated as white precipitate in 80-90% isolated yield after removal of solvent; B. J. Hathaway, D. G. Hohal, and J. D. Postlethwaite, J. Chem. Soc., 1961, 3215.

10) The quantum yield for the formation of **2a** ([**1**] = 0.1 mol/dm^3) is 0.2 ± 0.01.

11) Irradiation of trans-1-methyl-2-phenylcyclopropane and trans-1,2-diphenylcyclopropane in CH_3CN-MeOH(3:1) solutions under similar conditions afforded 1,3-dimethoxy-1-phenylbutane and 1,3-dimethoxy-1,3-diphenylpropane as a mixture of meso- and dl-isomers, respectively in 75-85% yields. However, in the case of 1-cyano-1-phenylcyclopropane or bicyclo[4.1.0]heptane, no cleaved product was obtained.

12) All new compounds obtained here afforded satisfactory spectral data and elemental analyses.

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14) The oxidation potentials were determined by cyclic voltammetry: Pt electrode: Electrolyte, tetraethylammonium perchlorate(0.1 mol/dm^3) in acetonitrile: Potentials(vs. Ag/Ag$^+$), **1**(1.38 V), **3**(1.51 V), **5**(1.23 V), DMB(0.95 V), TMB(1.03 V).

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