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CLEAVAGE OF CYCLOPROPANE RING VIA PHOTOINDUCED ELECTRON-TRANSFER BY THE USE OF COPPER(II) IONS[1)]

Kazuhiko MIZUNO, Jun OGAWA, Hirokazu KAGANO, and Yoshio OTSUJI
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591

Irradiation of a methanolic solution of phenylcyclopropane in the presence of copper(II) ions affords 1,3-dimethoxy-1-phenylpropane and meso- and dl-1,6-dimethoxy-3,4-diphenylhexanes in good yields through the electron-transfer from the excited cyclopropane to Cu(II) ions.

Phenylcyclopropane(**1**) can be cleaved oxidatively by metal ions such as Pb(IV), Tl(III), and Hg(II) in the presence of acetate ion.[2)] Direct photocleavage of polyaryl substituted cyclopropanes in protic media has also been reported.[3,4)] However, these reactions often afford several sorts of products which may be produced from different kinds of intermediates. Recently, the reactivity of arylcyclopropane cation radicals generated through photoinduced electron-transfer has received a considerable attention mainly from the mechanistic viewpoint. Very recently, Hixson's group and we have independently reported the photoinduced oxidative cleavage of phenylcyclopropanes in the presence of organic electron acceptor.[5)] We now report the photoinduced nucleophilic attack of methanol on **1** in the presence of copper(II) ions, which proceed via one-electron transfer from excited **1** to Cu(II) ions.

Irradiation of a methanolic solution of **1**(3 mmol) and copper(II) perchlorate hexahydrate(3 mmol) with a high-pressure mercury arc in quartz tube gave a mixture of 1,3-dimethoxy-1-phenylpropane(**2**) (70%, colorless oil), meso-1,6-dimethoxy-3,4-diphenylhexane(**3**) (3%, mp 81-83 °C), and its dl-isomer(**4**) (3%, colorless oil) along with metallic copper powder(70%), which was precipitated out during the reaction. The organic products were isolated by column chromatography on silica gel and their structures were determined by spectral data.

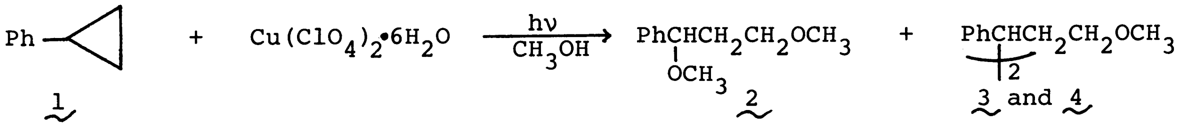

Table 1. Photoreaction of phenylcyclopropane(**1**) in the presence of Cu(II) ions[a)]

Cu(II)Compd	Yields of Products(%) **2**	**3** + **4**	**5**	Cu(II)Compd	Yields of Products(%) **2**	**3** + **4**	**5**
$Cu(ClO_4)_2{\cdot}6H_2O$	39	1	0	$Cu(NO_3)_2{\cdot}3H_2O$	3	0	0
$CuSO_4{\cdot}5H_2O$	43	4	0	$CuCl_2{\cdot}2H_2O$	1	0	0
$Cu(OTf)_2$	35	27	3				

a) Irradiation was carried out in quartz tube using **1**(0.8 mmol), Cu(II)compound (0.8 mmol) in 4 ml methanol. Yields are based on **1** used.

Copper(II) sulfate and trifluoromethanesulfonate(OTf) were also effective for this photocleavage reaction(Table 1). In the latter case, a mixture of 3 and 4 was obtained in nearly equal amount to 2, accompanied by a small amount of 3-methoxy-1-phenylpropane (5). Whereas, irradiation in the presence of copper(II) nitrate or chloride did not give 2, 3, and 4 in appreciable amounts. In all cases, the cleavage reaction was not observed in the dark.

Distribution of the products varied with the amount of added copper(II) perchlorate. Irradiation of 1 in the presence of one tenth equiv of copper(II) perchlorate gave 3 and 4 as major products(total yields; 11%) and the yield of 2 was reduced to 4% at ~15% conversion.

The pattern of this photoreaction can be explained in terms of the pathway involving one-electron transfer from excited 1 to Cu(II) followed by nucleophilic attack of methanol to the cation radical $1^{+\bullet}$(6).$^{6)}$ When the concentration of Cu(II) is high, the radical 6 is easily oxidized by Cu(II) to the cation 7 which is converted to 2 by nucleophilic attack of methanol. On the other hand, at low concentration of Cu(II), the dimers, 3 and 4, are predominantly formed by coupling of 6. Copper powder could be produced through disproportionation of copper(I) ions.

Similar irradiation of bicyclo[4.1.0]heptane or n-hexylcyclopropane in methanol gave no cleaved products in appreciable amounts. The photoinduced electron-transfer reactions from electron donating aromatic olefins such as styrene or N-vinylcarbazole to copper(II) perchlorate in polar media were reported.$^{7)}$ These results support the exothermic one-electron transfer mechanism from excited 1 to Cu(II), because the oxidation potentials of 1 and styrene are much lower than those of alkylcyclopropanes.$^{8)}$

$$1 \xrightarrow{h\nu} 1^{*} \xrightarrow{\mathrm{Cu(II)}} 1^{+\bullet} + \mathrm{Cu(I)} + \mathrm{ClO_4^-}$$

$$\begin{tikzcd}[column sep=large] 1^{+\bullet} \arrow[r, "-H^+", "CH_3OH"'] & \underset{6}{\mathrm{Ph\underset{\bullet}{C}HCH_2CH_2OCH_3}} \arrow[r, "\mathrm{Cu(II)}"] \arrow[dr, "\mathrm{coupling}"'] & \underset{7}{\mathrm{Ph\underset{+}{C}HCH_2CH_2OCH_3}} + \mathrm{Cu(I)} + \mathrm{ClO_4^-} \\ & & 3 + 4 \end{tikzcd}$$

$$7 \xrightarrow[\mathrm{CH_3OH}]{-\mathrm{H^+}} 2, \qquad 2\mathrm{Cu(I)} \longrightarrow \mathrm{Cu(0)}\downarrow + \mathrm{Cu(II)}, \qquad \mathrm{H^+} + \mathrm{ClO_4^-} \longrightarrow \mathrm{HClO_4}$$

References and Footnotes

1) The present work was partially supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education.
2) R.J.Quellette et al., J. Am. Chem. Soc., 90, 7064(1968) and references cited therein.
3) C.S.Irving et al., J. Am. Chem. Soc., 88, 5675(1966).
4) S.S.Hixson, J. Am. Chem. Soc., 96, 4866 and 4872(1974) and references cited therein.
5) V.R.Rao and S.S.Hixson, J. Am. Chem. Soc., 101, 6458(1979); K.Mizuno, J.Ogawa, and Y. Otsuji, The Annual Symposium on Photochemistry in Japan, Tokyo, 1979, p.116.
6) Possibility of innitiation by the excitation of very weak charge-transfer complex which can be formed at the ground state, followed by nucleophilic attack of methanol to excited complex such as [1···Cu(II)]*, has not been eliminated.
7) S.Murai and S.Tsutsumi, Bull. Chem. Soc. Jpn., 39, 198(1966); M.Asai, H.Matsui, and S. Tazuke, ibid., 47, 864(1974).
8) The oxidation potentials in acetonitrile vs. Ag/Ag$^+$ using a Pt electrode of 1, styrene, and bicyclo[4.1.0]heptane are 1.38, 1.47, and 1.83V, respectively.

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