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COPPER(II) SALT-ENHANCED VINYL CATION FORMATION IN THE PHOTOLYSIS OF VINYL BROMIDES

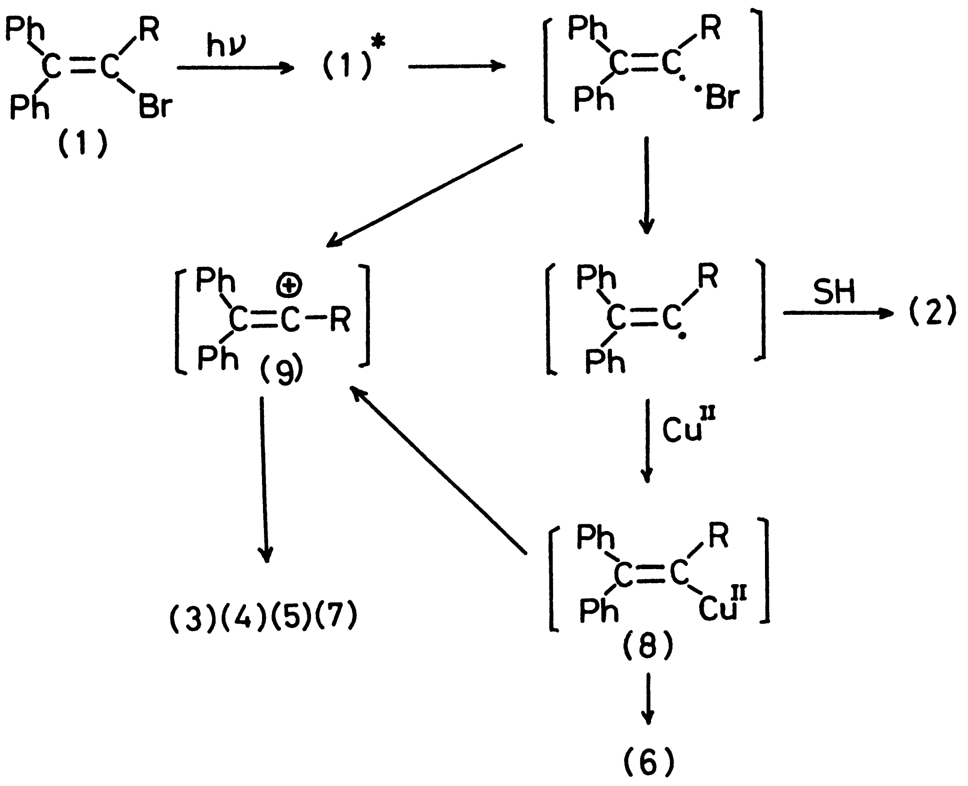
Tsugio KITAMURA, Shinjiro KOBAYASHI, and Hiroshi TANIGUCHI
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka 812

Irradiation of both 1,1-diphenyl-2-bromopropene(**1a**) and -ethylene (**1b**) in methanol in the presence of copper(II) salt resulted in the great increase of the yield of ionic products when compared to that without the salt. This suggests that cupric salt reacts with the vinyl radical, which is escaped from the solvent cage, to give ionic species via vinylcopper intermediate(**8**).

We found that the photolysis of aryl-substituted vinyl halides gave vinyl cations along with vinyl radicals.1) We wish to report here that the vinyl radical can be oxidized to ionic species by copper(II) salt.

Irradiation of **1a** (2 mmol) in methanol containing pyridine(0.2 ml) with a 100-W high-pressure Hg lamp under nitrogen atmosphere at 5 °C for 2 h led to the formation of 1,1-diphenylpropene(**2a**)(29%),2),3) 1,1-diphenylallene(**3**)(16%), and 9-methoxy-10-methylphenanthrene(**4**)(15%). Contrary to this, when the irradiation was carried out in the presence of cupric acetate(2 mmol) for 4 h, the radical product(**2a**) could not be detected. Along with **3** (28%) and **4** (5%), there were obtained E- and Z-1,2-diphenyl-1-methoxypropenes(**5a**)(23%), the precursor of **4**, and 1,1-diphenyl-2-methoxypropene(**6a**)4)(23%). The similar copper effect was observed in the photolysis of **1b**. Thus, without cupric acetate, 1,1-diphenylethylene(**2b**)(32%), diphenylacetylene(**7**)(24%), and E- and Z-1,2-diphenyl-1-methoxyethylenes(**5b**)(18%) were obtained.5) When an equivalent amount of cupric acetate was added, the yield of the radical product(**2b**) decreased from 32% to 23% and those of **7** and **5b** were 38% and 33%, respectively. 1,1-Diphenyl-2-methoxyethylene(**6b**) was detected in 4% yield. When 5 mol equivalents of cupric acetate were added, the yield of **2b** further decreased to 17%, and those of **7**, **5b**, and **6b** were 42, 33, and 4%, respectively.

The fact that the copper(II) salt inhibits or decreases the formation of **2** indicates that the vinyl radical escaped from the solvent cage is captured by copper(II) salt to form an organocopper intermediate(**8**).6) Then the electron transfer oxidation of **8** results in the formation of vinyl cation(**9**). The formation of **6** which might be ligand transfer is characteristic of the photolysis in the presence of copper(II) salt.7)



References and Notes

1) T.Suzuki, T.Sonoda, S.Kobayashi, and H.Taniguchi, J.C.S.,Chem.Commun., 1976, 180; S.A.McNeely and P.J.Kropp, J.Am.Chem.Soc., 98, 4319(1976).
2) Propene(**2a**) and (**2b**) were identified by comparison with authentic samples. The IR and NMR spectra of allene(**3**) were identical with the data in the literature[P.Beltrame, D.Pitea, A.Marzo, and M.Simonetta, J.Chem.Soc.(B), 1967, 71]. Phenathrene(**4**): mp 48-50 °C, picrate mp 135.5-137.5 °C; NMR (δ,$CDCl_3$) 2.65(s,3H), 3.90(s,3H), and 7.48-8.72(m,8H); MS(m/e) 222(M^+); UV λ_{max}(log ε) 223(4.21), 248(4.62), 255(4.71), 271(4.21), 278(4.06), 288 (3.95), 300(4.01), 322(2.43), 337(2.73), and 353(2.81); Found: C, 86.75; H, 6.41%; Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%.
3) Based on the consumed bromide in the range from 50 to 80% conversion.
4) Vinyl ethers(**5a** and **6a**) were confirmed by the hydrolysis to the ketones(**5a'** and **6a'**); (**6a'**): NMR(δ,CCl_4) 1.46(d,J=7Hz,3H), 4.48(q,J=7Hz,1H), and 7.12-7.89(m,10H); IR 1681 cm^{-1}(C=O), (**5a'**): NMR(δ,CCl_4) 2.21(s,3H), 4.96(s,1H), and 7.16(s,10H); IR 1712 cm^{-1}(C=O).
5) **2b**, **7**, **5b**, and **6b** were identified by comparison with authentic samples.
6) J.K.Kochi, "Free Radicals", Vol.I, J.K.Kochi, Ed.Wiley-Intersciences, New York, N.Y., 1973, Chapt.11 and references therein.
7) In organocopper intermediate(**8**), methanol may coordinate with copper ion.

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