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Photolysis of Vinyl Halides. Preferential Formation of Vinyl Cations by Copper(II) Salts

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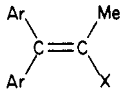
Abstract: Photolysis of vinyl halides in the presence of copper(II) salts resulted in a significant suppression of product formation derived from vinyl radicals. Photolysis of 1,1-diaryl-2-bromopropenes in the presence of copper(II) salts yielded no 1,1-diaryl-2-propenes. Photolysis of other vinyl halides, i.e., 1,1-diaryl-2-iodopropenes, 1,1-diaryl-2-bromoethylenes, and 1-bromo-2-(p-methoxyphenyl)ethylene, also led to a large decrease in the yields of the reduced olefins derived from the vinyl radicals. Copper(II) triflate was found to be more effective for the oxidation of vinyl radicals than copper(II) acetate. These reactions are explained by the intervention of vinylcopper intermediates and the formation of vinyl cations.

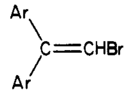
Recently much attention has been paid to the photochemical cleavage of the carbon–halogen bond in organic halides,[1] generating reactive intermediates. In the photolysis of vinyl halides,[2] two kinds of reactive intermediates, i.e., vinyl cations and vinyl radicals, are produced, as shown in Scheme I. Vinyl cations are preferentially generated by use of stabilizing substituent and a halogen atom with a high electron affinity.[3] However, in the absence of such stabilization, vinyl cations are usually not formed as the initially generated vinyl radicals are too reactive and form reduced products by the abstraction of a hydrogen atom.[3] Therefore, in order to produce vinyl cations preferentially in such cases, it is necessary to oxidize the initially formed vinyl radical to the corresponding vinyl cation. For this purpose, copper(II) salts are suitable.[4] In a preliminary study we reported that the vinyl radical products decreased and the vinyl cationic products increased in the photolysis of vinyl bromides in the presence of copper(II) acetate.[5] In this paper we discuss in full detail the photolysis of vinyl halides in the presence of copper(II) salts and the concomitant generation of vinyl cations.

Results

The vinyl halides used in this study were α-methyl-substituted vinyl halides **1** and α-unsubstituted vinyl halides **7** and **12**. These halides gave predominantly the radical products in the usual photolysis in the absence of copper(II) salts. Each system will be described in detail.



1a: Ar = Ph
1b: Ar = An

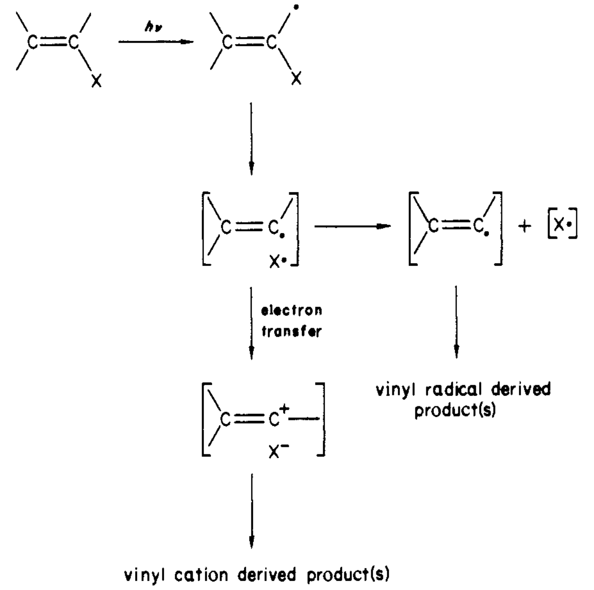


7a: Ar = Ph
7b: Ar = An

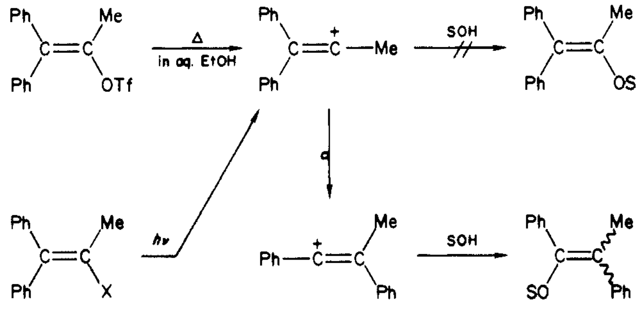
AnCH═CHBr
12

X = Br, I; An = p-MeOC$_6$H$_4$

Scheme I



Scheme II



Photolysis of 1,1-Diaryl-2-halopropenes 1 in the Presence of Copper Salts. As reported previously,[3] irradiation of 1,1-diphenyl-2-bromopropene (**1a**) in methanol containing pyridine as a buffer gave 1,1-diphenylpropene (**2a**), 1,1-diphenylallene (**3a**), and 9-methoxy-10-methylphenanthrene (**6a**). Propene **2a** is derived from the vinyl radical and allene **3a** and phenanthrene **6a** are from the corresponding vinyl cations.

Addition of copper(II) acetate showed a drastic effect on the product distribution from the photolysis of vinyl bromide **1a–Br**. Photolysis of **1a–Br** in the presence of copper(II) acetate afforded no propene **2a** but resulted in allene **3a**, phenanthrene **6a**, and new products that were assignable to vinyl ethers **4a** and **5a**–E and –Z on the basis of their properties and by independent syntheses.

The formation of the unrearranged vinyl ether **4a** is especially characteristic of the photolysis in the presence of copper salts because unrearranged vinyl ethers like **4a** have never been observed

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[2] (a) Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 180. (b) McNeely, S. A.; Kropp, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 4319–4320. (c) Sket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans 1* **1979**, 752–756. (d) Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907–6914.

[3] (a) Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1982**, *47*, 2323–2328. (b) Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Fiakpui, C. Y.; Lee, C. C.; Rappoport, Z. *J. Org. Chem.* **1984**, *49*, 3167–3170.

[4] (a) Kochi, J. K. *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, Chapter 11. (b) Kochi, J. K. *Organometallic Mechanisms* and *Catalysis*; Academic Press: New York, 1978; Chapter 2.

[5] Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1978**, 1223–1224.

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Table I. Photolysis of Vinyl Halide **1** in the Presence of Copper(II) Salts

vinyl halide **1**				yield,[c] %				
Ar	X	copper(II) salt[a]	conv, %	**2**	**3**	**4**	**5**	**6**
Ph	Br		84	29	16	0	0	15
		$Cu(OAc)_2$	71	0	28	23	23	5
		$Cu(OAc)_2$[b]	89	0	30	9	23	11
		$Cu(OTf)_2$	89	0	26	2	16	25
		$Cu(OMe)_2$	64	0	40	2	26	10
Ph	I		100	46	26	0	0	2
		$Cu(OAc)_2$	82	17	38	29	3	1
		$Cu(OTf)_2$	67	10	64	2	2	3
An	Br		87	19	10	0	0	36
		$Cu(OAc)_2$	84	0	21	3	21	30
		$Cu(OTf)_2$	81	0	24	0	23	31
An	1		65	49	16	0	9	6
		$Cu(OAc)_2$	77	12	20	29	0	9
		$Cu(OTf)_2$	73	5	40	0	8	22

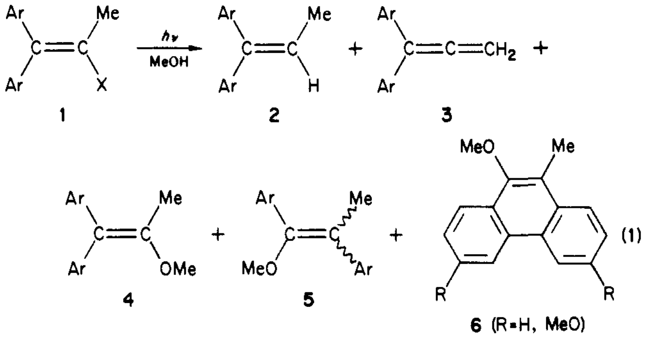
[a] A slight excess of pyridine was added as a buffer. [b] Pyridine was absent. [c] On the basis of the consumed halide **1**.

Table II. Photolysis of Vinyl Bromide **7** in the Presence of Copper(II) Salts

vinyl bromide **7** Ar	copper salt[a,d]	conv, %	yield,[b] % **8**	**9**	**10**	**11**
Ph		63	32	0	18	24
	$Cu(OAc)_2$	53	23	4	33	38
	$Cu(OAc)_2$[c]	53	17	4	33	42
	$Cu(OTf)_2$	71	8	0	27	63
An		74	10	0	39[e]	12
	$Cu(OAc)_2$	62	4	0	55[e]	15
	$Cu(OTf)_2$	59	2	0	55[e]	17

[a] A slight excess of pyridine was added as a buffer. [b] On the basis of the consumed bromide **7**. [c] Five equivalent moles of copper(II) acetate. [d] An equivalent mole of copper salt. [e] Yields were determined from those of 4,4′-dimethoxybenzyl phenyl kentone which was formed by acid hydrolysis of **10b**.

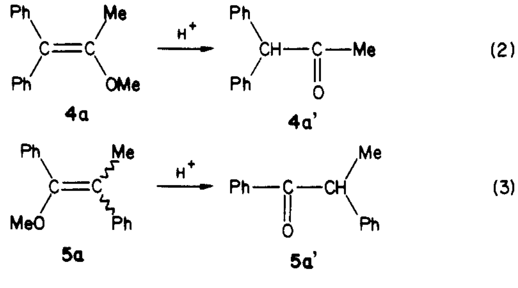
in normal photolysis[3] and solvolysis[6] of α-methyl-β,β-diphenylvinyl systems, where only 1,2-phenyl migrated products are formed (Scheme II). The formation of the vinyl ethers **5a**-***E*** and **-*Z*** with a 1,2-phenyl migrated skeleton, the precursor of the phenanthrene **6a**, is due to the filter effect by the copper salts on photocyclization of **5a**. The yields and distribution of the products are given in Table I.



In control experiment carried out in the dark, the starting material was recovered unchanged, indicating that the reaction is initiated by the photoexcitation of vinyl halides **1**.

Copper(II) triflate, $Cu(OTf)_2$, and copper(II) methoxide, $Cu(OMe)_2$, also showed similar effects to cupric acetate. In both cases, no propene **2a** was observed. However, with photolysis in the presence of copper(II) triflate the yield of the vinyl ether **4a**, which was 23% with cupric acetate, decreased to 2% and the yield of phenanthrene **6a** increased. Because of the better transparency of $Cu(OTf)_2$ compared to $Cu(OAc)_2$ the permeability of the solution to light facilitated the photocyclization and enhanced the formation of **6a**. Copper(II) methoxide, in contrast, increased the formation of allene **3a**.

Pyridine also affected the product distribution of the photolysis in the presence of cupric salts. In the absence of pyridine photolysis with copper(II) acetate decreased the yield of the unrearranged vinyl ether **4a**. However, photolysis in the presence of copper(II) triflate requires pyridine because otherwise the liberated trifluoromethanesulfonic acid hydrolyzes the vinyl ethers **4a** and **5a** to ketones **4a′** and **5a′**. Therefore, photolysis in the presence of $Cu(OTf)_2$ was always carried out with pyridine as a buffer.



Normal photolysis of vinyl iodide **1a–I** gives the highest yield of radical-derived product **2a**.[3] Irradiation of the vinyl iodide **1a–I** in the presence of various copper(II) salts gave propene **2a**, allene **3a**, vinyl ethers **4a** and **5a**, and phenanthrene **6a** as products. As expected, copper(II) triflate resulted in a larger depression on the formation of radical product **2a** than cupric acetate. Moreover, compared to the vinyl bromide **1a–Br**, the vinyl iodide **1a–I** gave mainly unrearranged products, suggesting that the counteranion also affects the product distribution.

Although the β-substituent generally has only a minor effect in the solvolysis of vinyl derivatives,[7] irradiation of vinyl bromide **1b–Br** and vinyl iodide **1b–I**, respectively, in the presence of copper(II) salts showed a remarkable effect of β-substituent as well as the normal photolysis.[3] The previous discussion on the β-substituent effect is applicable here as well.[3]

Photolysis of 1,1-Diphenyl-2-bromoethylene (7) in the Presence of Copper(II) Salts. Photolysis of α-unsubstituted vinyl halides is particularly interesting because the reactivity of the resulting vinyl radicals and cations should be very high.

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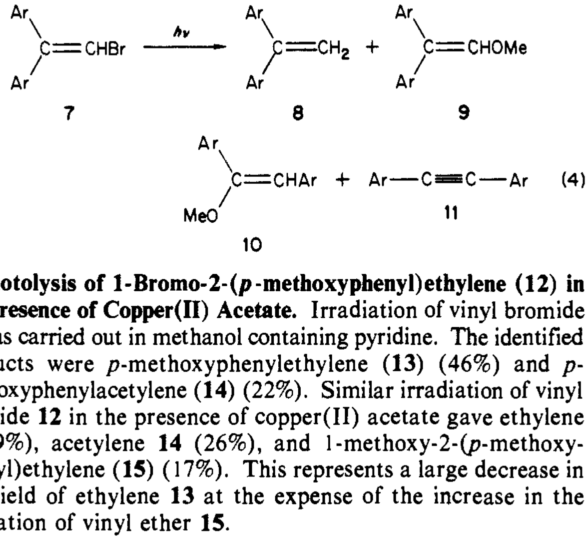
Table III. Comparison of Photolysis in the Absence and Presence of Copper(II) Salt

vinyl halide	ratio of radical products to nonradical products: absence of Cu^{II} salt	presence of Cu^{II} salt[a]	
1a	29:31	$Cu(OAc)_2$	0:79
		$Cu(OTf)_2$	0:69
		$Cu(OMe)_2$	0:78
1b	19:46	$Cu(OAc)_2$	0:75
		$Cu(OTf)_2$	0:78
7a	32:42	$Cu(OAc)_2$	23:75
			17:79[b]
		$Cu(OTf)_2$	8:90
7b	10:51	$Cu(OAc)_2$	4:70
		$Cu(OTf)_2$	2:72
12	46:22	$Cu(OAc)_2$	9:43

[a] In the presence of an equimolar copper(II) salt. [b] In the presence of 5 equivalent moles of copper(II) acetate.

Normal irradiation of vinyl bromide **7a** in methanol containing pyridine as a buffer gave 1,1-diphenylethylene (**8a**), 1,2-diphenyl-1-methoxyethylene (**10a**), and 1,2-diphenylacetylene (**11**). Ethylene **7a** is probably derived from the vinyl radical, and vinyl ethers **10a** and acetylene **11a** result from the corresponding vinyl cation.

The results of the photolysis of vinyl bromide **7a** in the presence of copper(II) salts are given in Table II. The products obtained are the same as those in the photolysis without copper(II) salts, except for a small amount of 1-methoxy-2,2-diphenylethylene (**9a**) and in significant differences in the product ratio (radical vs. nonradical products). Once again copper(II) triflate showed a large depressing effect on the radical product formation compared to that of copper(II) acetate. The relatively small effect of copper(II) salt in the photolysis of vinyl bromide **7b** is attributed to the small amounts of radical products in the photolysis without copper(II) salt.



(4)

Photolysis of 1-Bromo-2-(*p*-methoxyphenyl)ethylene (12) in the Presence of Copper(II) Acetate. Irradiation of vinyl bromide **12** was carried out in methanol containing pyridine. The identified products were *p*-methoxyphenylethylene (**13**) (46%) and *p*-methoxyphenylacetylene (**14**) (22%). Similar irradiation of vinyl bromide **12** in the presence of copper(II) acetate gave ethylene **13** (9%), acetylene **14** (26%), and 1-methoxy-2-(*p*-methoxyphenyl)ethylene (**15**) (17%). This represents a large decrease in the yield of ethylene **13** at the expense of the increase in the formation of vinyl ether **15**.

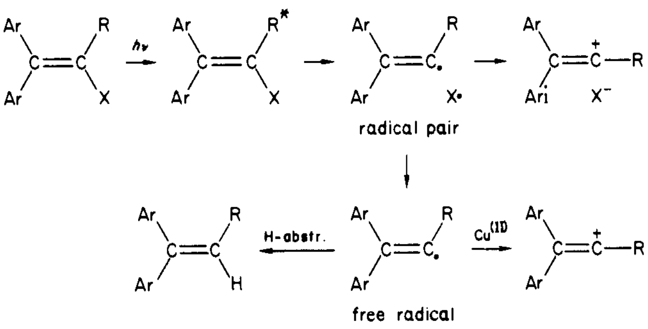
$$\underset{\mathbf{12}}{\mathrm{AnCH{=}CHBr}} \xrightarrow{h\nu} \underset{\mathbf{13}}{\mathrm{AnCH{=}CH_2}} + \underset{\mathbf{14}}{\mathrm{AnC{\equiv}CH}} + \underset{\mathbf{15}}{\mathrm{AnCH{=}CHOMe}} \quad (5)$$

$$\mathrm{An} = p\text{-}\mathrm{MeOC_6H_4}$$

Discussion

Effect of Copper(II) Salts on Product Distribution. Generally normal photolysis of vinyl halides gives both radical-derived and ionic-derived products. This holds in the case of photolysis in the presence of copper(II) salts as well. Hence, the products from the photolysis can be divided into two classes: (i) the radical-derived product(s) and (ii) the nonradical-derived product(s) formed from vinyl cations and/or organocopper intermediates.

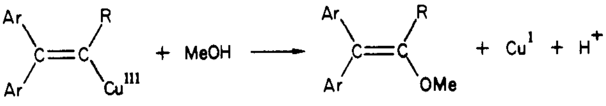
Scheme III



A comparison of products from photolysis in the presence of copper(II) salts with that in the absence of copper(II) salts is given in Table III.

As seen from the data, photolysis of α-methylvinyl bromides **1a-Br** and **1b-Br** in the presence of Cu(II) salts leads to the complete suppression of radical-derived products, and photolysis of vinyl iodides **1a-I** and **1b-I** and primary vinyl bromides results in a large decrease of the radical-derived products.

Mechanistic consideration will focus on the effect of copper(II) salts in the photolysis of vinyl halides. The first step is the homolysis of the carbon–halogen bond in the excited vinyl halide to form the vinyl radical–halogen atom pair. The second step contains two competing processes, i.e., (1) a single electron transfer occurs in the radical pair to form a vinyl cation–halogen anion pair and (2) the radicals may escape from the solvent cage to give free vinyl radicals. The third step is the reaction of the free vinyl radical with the copper(II) salt, which, however, competes with the abstraction reaction of a hydrogen atom by the radical from the solvent. Therefore, the primary effect of copper(II) salts in the photolysis of vinyl halides is attributed to trapping of the free vinyl radical by the copper(II) salts and their oxidation by the cupric ions. Oxidation of the vinyl radical by the copper(II) salt most likely proceeds via a vinylcopper intermediate formed by reaction of the initially formed vinyl radical with copper(II).[4b] The intervention of such a vinylcopper intermediate is suggested by the formation of unrearranged vinyl ethers which are only formed in the photolysis with copper(II) salts. The alternative formation of the unrearranged vinyl ethers by reaction of the initially formed (unrearranged) vinyl cation with methanol may be ruled out by the relative instability of this vinyl cation that is known to undergo a 1,2-aryl shift across the double bond to produce a more stable α-arylvinyl cation before nucleophilic attack by methanol.[3,6] Likewise, since the single-step (direct S_N2) displacement in vinylic systems is unknown[8] due to its high energy, the formation of the unrearranged vinyl ethers is most consistent with the intermediacy of a vinylcopper intermediate.[9]



(6)

The sequel of the reaction of the vinyl radical with the copper(II) ion is discussed as follows (Scheme IV). The unrearranged vinyl ethers **4** and **9** should derived from the vinylcopper intermediate **20**. The allene **3** is formed by oxidative elimination from the vinylcopper intermediate **20** as well as by deprotonation from the α-methylvinyl cation **21** which is formed by heterolysis of the carbon–copper bond. The vinyl ethers with the 1,2-aryl rearranged skeleton are derived from the vinyl cation **21** followed by a 1,2-aryl shift and nucleophilic trapping of vinyl cation **22**. Acetylene **11** is formed by deprotonation of the rearranged vinyl cation **22**. The enhanced yields of the nonradical-derived products in the photolysis

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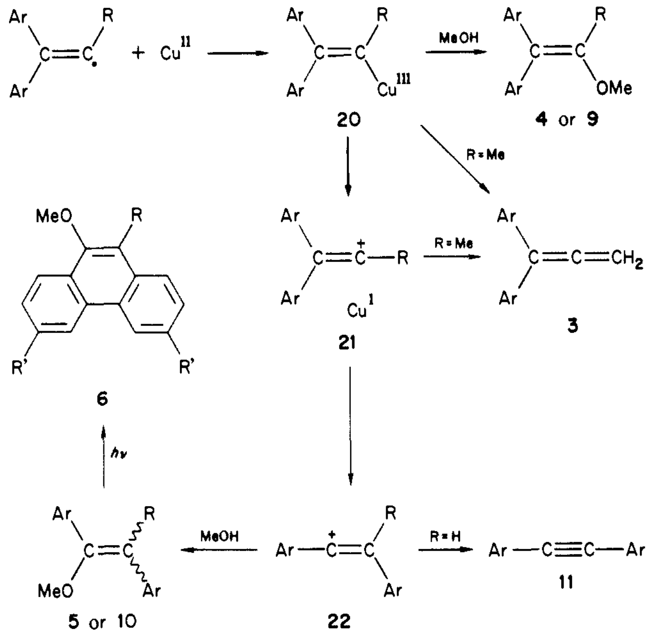
[8] Reference 7; p 215.

[9] Such a direct displacement was also observed in the copper(II) oxidation of organopentafluorosilicates. See: Yoshida, J.; Tamao, K.; Kakui, T.; Kurita, A.; Murata, M.; Yamada, K.; Kumada, M. *Organometallics* **1982**, *1*, 369–380.

Scheme IV



with copper(II) salts are attributed to the oxidation of the vinyl radicals by copper(II) salts.

Effect of Ligand. In the case of α-methylvinyl bromides **1**, both copper(II) triflate and acetate gave rise to the exclusive formation of nonradical products. However, in other cases, an effect of the ligand on the copper(II) was observed on the reactions.

Copper(II) triflate was found to be more effective for the oxidation of the vinyl radicals than copper(II) acetate. As reported by Jenkins and Kochi,[10] the degree of dissociation between the ligand and the copper ion is important in the oxidation of alkyl radicals by copper(II) salts. In the cases of the vinyl bromide **7** and the vinyl iodide **1-I**, copper(II) triflate led to a greater decrease in the yield of the radical products compared with copper(II) acetate. In a vinylcopper intermediate, the triflate ion coordinates with the copper less strongly than the acetate ion[10] and hence favors the heterolysis of the copper–carbon bond (i.e., formation of a vinyl cation) to the oxidation elimination (i.e., formation of allene **3**).[11]

Copper(II) methoxide also has the ability to oxidize vinyl radicals to cations similar to that of copper(II) acetate. The characteristics of copper(II) methoxide is the increase in yield of allene **3**. This is attributed to the basicity of the ligand. In the vinylcopper intermediate the highly basic ligand favors a synchronous elimination,[12] resulting in a larger amount of allene **3**.

Element Effect. Photolysis of the vinyl iodides tends to give more unrearranged products, i.e., allene **3** and vinyl ether **4**, compared with that of the vinyl bromides. This may be due to a halogen element effect where the iodide ion stabilizes the vinylcopper intermediate by better coordination and therefore may facilitate the oxidative elimination to allene and the displacement by methanol.

In summary, we have observed a novel effect of Cu(II) upon the photolysis of vinyl halides. As the data show there is a significant difference in the kind of products and their ratio, dependent upon both the type of Cu(II) salt used and the leaving group of the vinyl halide. In particular, radical-derived products are eliminated or significantly diminished in the presence of Cu(II) salts compared to normal photolysis. This is attributed to the capture of the initially formed vinyl radical by the copper species and its subsequent oxidation to the corresponding vinyl cation or formation of a novel vinylcopper(III) intermediate that yields the typical known vinyl cation derived products and new ones derived from the vinylcopper(III) intermediate. Copper(II) triflate was found to be more effective in the capture of the initially formed radical than copper(II) acetate, whereas copper(II) methoxide was found to give the greatest amount of elimination products.

Experimental Section

Melting points are uncorrected. NMR spectra were taken with a HITACHI R-24B spectrometer. Mass spectra were obtained with a JEOL JMS-07 spectrometer. IR spectra were recorded with a Shimadzu IR-400 spectrometer. Gas chromatography was performed with a Shimadzu gas chromatograph GC-6A. High-performance liquid chromatography was carried out with a 635-HITACHi liquid chromatograph.

Vinyl bromides were prepared by the methods described in the literatures: **1a-Br**,[13] **1a-I**,[3a] **1b-Br**,[14] **1b-I**,[3a] **7a**,[15] **7b**,[14] and **12**.[16] Copper(II) acetate was obtained commercially. Copper(II) triflate[10] and copper(II) methoxide[17] were prepared by the literature methods.

Photolysis was carried out in an immersion-type water-cooled photoreactor equipped with a high-pressure mercury lamp (100 W). Irradiation of the vinyl halide (1.0×10^{-2} mol·dm^{-3}) in methanol containing pyridine (1.3×10^{-2} mol·dm^{-3}) was carried out in the absence and presence of the copper(II) salt (1.0×10^{-2} mol·dm^{-3}) under a nitrogen atmosphere at 5 °C. The photolysis in the case of copper(II) triflate was carried out at a concentration of 3.7×10^{-2} mol·dm^{-3} of pyridine. After irradiation the solvent was evaporated and the residue was passed through a short column of alumina with benzene–ether as eluant for removal of the pyridinium salt and the copper salts. The products eluted were separated by column chromatography on alumina and identified on the basis of their acid hydrolyses and spectral data. The yields of the products were determined by NMR with an internal standard, *tert*-butylbenzoic acid, or by GC.

Photolysis of 1,1-Diphenyl-2-halopropene (1a). A normal irradiation of the vinyl halide **1a** in methanol gave 1,1-diphenylpropene (**2a**),[13] 1,1-diphenylallene (**3a**),[18] and 9-methoxy-10-methylphenanthrene (**4a**),[3a] which were reported previously.[3a]

Irradiation of **1a** in the presence of a copper(II) salt was carried out in the manner described above. The NMR spectrum of the crude reaction mixture showed absence of propene **2a**, except for irradiation of the vinyl iodide **1a-I**, but allene **3a**, phenanthrene **4a**, and new products having three kinds of singlet peaks at both methyl (at 1.91, 1.93, and 2.13 ppm) and methoxyl (at 3.21, 3.38, and 3.51 ppm) resions, respectively, to be assigned to vinyl ethers **4a** (*E*)- and (*Z*)-**5a**. As these vinyl ethers could not be separated by column chromatography on alumina, the crude reaction mixture obtained by irradiation of **1a-Br** (2 mmol) in the presence of copper(II) acetate was hydrolyzed to confirm the vinyl ethers with 2 mL of concentrated hydrochloric acid and 50 mL of methanol. After being stirred at a room temperature overnight, the products were extracted with ether and washed with water, and the organic layer was dried over anhydrous sodium sulfate. After evaporation of the ether the residue was submitted to column chromatography on alumina. Elution with benzene gave 2-phenylpropiophenone:[19] NMR (CCl_4) δ 1.45 (d, J = 7 Hz, 3 H, CH_3), 4.47 (q, J = 7 Hz, 1 H, CH), and 7.05–7.80 (m, 10 H, ArH); IR 1682 cm^{-1} (C=O). Elution with ether gave 2,2-diphenylacetone:[20] NMR (CCl_4) δ 2.21 (s, 3 H, CH_3), 4.96 (s, 1 H, CH), and 7.16 (s, 10 H, ArH); IR 1712 cm^{-1} (C=O). Therefore, new peaks in the crude NMR spectrum were attributed to those of vinyl ethers **4a**, (*E*)- and (*Z*)-**5a**. Furthermore, the signals at δ 1.93 (CH_3) and 3.21 (OCH_3) were assigned to those of (*Z*)-**5a**, and the signals at δ 2.13 (CH_3) and 3.38 (OCH_3) were to those of (*E*)-**5a** by comparison with independently obtained vinyl ethers (*E*)- and (*Z*)-**5a** from photolysis of 1-bromo-1,2-diphenylpropene in methanol, as described later. Consequently, other signals at δ 1.91 (CH_3) and 3.51 (OCH_3) were assigned to those of vinyl ether **4a** where the phenyl group was not migrated.

Photolysis of 1,11-Bis(*p*-methoxyphenyl)-2-halopropene (1b). A normal irradiation of vinyl halide **1b** in methanol gave 1,1-bis(*p*-methoxyphenyl)propene (**2b**),[14] 1,1-bis(*p*-methoxyphenyl)allene (**3b**),[3a] and 3,6,9-trimethoxy-10-methylphenanthrene (**6b**),[3a] as reported previously.[3a]

Similarly irradiation of **1b** in the presence of a copper(II) salt gave three kinds of vinyl ethers **4b**, (*E*)- and (*Z*)-**5b** together with **2b**, **3b**, and

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(10) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843–855.

(11) Formation of allene 3 is also involved in the path via a vinyl cation.

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6b. The vinyl ethers (*E*)- and (*Z*)-**5b** [(*E*)-**5b**: δ ($CDCl_3$) 2.10 (s, CH_3), 3.34 (s, OCH_3). (*Z*)-**5b**: δ ($CDCl_3$) 1.89 (s, CH_3), 3.08 (s, OCH_3)] could not be obtained purely but could be identified easily by comparison with (*E*)- and (*Z*)-**5a** and by acid hydrolysis with concentrated hydrochloric acid and methanol to α-methylanisoin:[21] NMR ($CDCl_3$) δ 1.47 (d, *J* = 7 Hz, 3 H, CH_3), 3.71 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 4.55 (q, *J* = 7 Hz, 1 H, CH), and 6.67–7.94 (m, 8 H, ArH); IR 1670 cm^{-1} (C=O). Vinyl ether **4b** [δ (CCl_4) 1.86 (s, CH_3), 3.47 (s, OCH_3), 3.69 (s, OCH_3), 3.72 (s, OCH_3), and 6.56–7.24 (m, ArH)] was separated rather purely by column chromatography on alumina in the case of irradiation of **1b-I** with copper(II) acetate and was confirmed by conversion to 2,2-bis(*p*-methoxyphenyl)acetone with concentrated hydrochloric acid and methanol, mp 67–69 °C (EtOH). NMR δ (CCl_4) 2.10 (s, 3 H, CH_3), 3.72 (s, 6 H, OCH_3), 4.84 (s, 1 H, CH), and 6.62–7.08 (m, 8 H, ArH). IR 1710 cm^{-1} (C=O). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.12; H, 6.79.

A control experiment was carried out in the absence of light. A mixture of vinyl bromide **1a-Br** (1 mmol), copper(II) acetate (1 mmol), pyridine (0.1 mL), and methanol (100 mL) was stirred at room temperature under a nitrogen atmosphere for 15 h in the dark. After evaporation of the solvent, the residue was extracted with ether, and the organic layer was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate. After evaporation of the ether, the NMR spectrum showed no change and the vinyl bromide **1a-Br** was recovered unchanged.

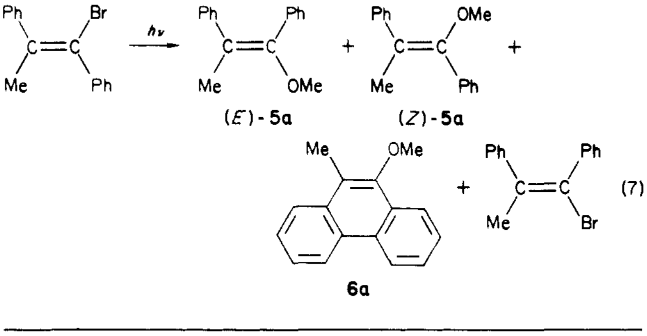
Photolysis of 1,1-Diaryl-2-bromoethylene (7). A solution of vinyl bromide **7a** in methanol containing pyridine was irradiated in the presence or absence of a cupric salt in the manner described above. The products were analyzed by NMR and GC (column OV-17, 0.5 m, 170 °C). The products are as follows. 1,1-Diphenylethylene (**8a**):[22] NMR δ (CCl_4) 5.34 (s, 2 H, CH_2) and 7.20 (s, 10 H, ArH). 2-Methoxy-1,1-diphenylethylene (**9a**):[23] NMR δ (CCl_4) 3.16 (s, 3 H, OCH_3), 6.22 (s, 1 H, CH), and 7.06 (s, 10 H, ArH). (*E*)- (*Z*)-1-methoxy-1,2-diphenylethylenes ((*E*)- and (*Z*)-**10a**):[24] NMR δ (a mixture of (*E*)- and (*Z*)-**10a** in $CDCl_3$) 3.68 (s, OCH_3, (*E*)), 5.72 (s, CH, (*E*)), 3.52 (s, OCH_3, (*Z*)), 6.00 (s, CH, (*Z*)), and 6.91–7.70 (m, ArH, (*E*) and (*Z*)). (*E*)- and (*Z*)-**10a** were confirmed by comparison with the authentic samples which were prepared independently by Freeman and Johnson's method.[24] 1,2-Diphenylacetylene (**11a**): mp 55–58 °C (lit.[25] mp 61.5–62.5 °C). NMR δ (CCl_4) 7.08–7.63 (m, ArH).

Vinyl bromide **7b-Br** in methanol was irradiated similarly. Since one of the products, 1,2-bis(*p*-methoxyphenyl)-1-methoxyethylene (**10b**), was unstable and hydrolyzed to 4,4′-dimethoxybenzyl phenyl ketone (**10b′**) during workup or on column chromatography, workup was performed as follows. After irradiation, the solvent was evaporated and to the residue was added 10 mL of 2 mol·dm^{-3} hydrochloric acid with stirring for 5 min. The products were extracted with ether, and the organic layer was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate. After evaporation of the solvent, the products were analyzed by NMR and GC (column OV-17, 0.5 m, 200 °C). The yield of **10b** was determined from that of **10b′**. The products are as follows. 1,1-Bis(*p*-methoxyphenyl)ethylene (**8b**), mp 138–142 °C (lit.[14] mp 142–143 °C): NMR δ (CCl_4) 3.78 (s, 6 H, OCH_3), 5.20 (s, 2 H, CH_2), and 6.67–7.27 (m, 8 H, ArH). 4,4′-Dimethoxybenzyl phenyl ketone (**10b′**), mp 110–112 °C (lit.[26] mp 108–109 °C): NMR δ (CCl_4) 3.68 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.98 (s, 2 H, CH_2), and 6.56–7.85 (m, 8 H, ArH). 1,2-Bis(*p*-methoxyphenyl)acetylene (**11b**), mp 143–144 °C (lit.[27] mp 142–143 °C): NMR δ ($CDCl_3$) 3.81 (s, 6 H, OCH_3), 6.83 (d, *J* = 9 Hz, 4 H, ArH), and 7.43 (d, *J* = 9 Hz, 4 H, ArH).

Photolysis of 1-Bromo-2-(*p*-methoxyphenyl)ethylene (12). After similar irradiation, the products were analyzed by HPLC (stainless steel 2.6 × 500 mm, HITACHI No. 3010, methanol elution, flow rate 1 mL/min) with detection at 254 nm. *p*-Methoxystyrene (**13**)[28] (retention time 7.2 min) and *p*-methoxyphenylacetylene (**14**)[29] (retention time 5.5 min) were prepared independently by the methods described in the literature. 1-(*p*-Methoxyphenyl)-2-methoxyethylene (**15**) (retention time 8.3 min) was synthesized independently by the procedure of Wittig and Schlosser,[23] Kugelrohr distillation, 170 °C (oven temp)/2.67 × 10^3 Pa.

Photolysis of 1-Bromo-1,2-Diphenylpropene. 1-Bromo-1,2-diphenylpropene was prepared by a modified method of the conventional bromination of 1,2-diphenylpropene. To a solution of 1,2-diphenylpropene[30] (9.71 g, 50 mmol) in carbon tetrachloride (70 mL) was added dropwise a solution of bromine (2.57 mL) in carbon tetrachloride (39 mL) with stirring at 0 °C. After the completion of bromination 40 mL of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added slowly. Then, the carbon tetrachloride was evaporated, 100 mL of benzene was added, and the benzene solution was refluxed for 1 h. The reaction mixture was poured into water and extracted with ether–benzene, and the organic layer was washed with water, and saturated sodium chloride solution and dried over anhydrous sodium sulfate. After evaporation of the solvent the crude products were submitted to column chromatography on alumina. 1-Bromo-1,2-diphenylpropene[31] was obtained as a 2:1 mixture of (*E*)- and (*Z*)-isomers with a benzene–hexane eluate. Yield, 10.81 g (79%). (*E*)-Isomer recrystallized from EtOH isomerized to (*Z*)-isomer at ca 140 °C and melted at 158–159 °C. (*E*)-Isomer: NMR δ (CCl_4 2.34 (s, 3 H, CH_3), 6.90 (s, 5 H, ArH), and 6.95 (s, 5 H, ArH). (*Z*)-Isomer: mp 158–159 °C (EtOH). NMR δ (CCl_4) 1.95 (s, 3 H, CH_3) and 7.05–7.40 (m, 10 H, ArH).

Irradiation of (*Z*)-1-bromo-1,2-diphenylpropene (1 mmol) was carried out in methanol (100 mL) and methylene chloride (20 mL) containing pyridine (0.1 mL) as a buffer through a Pyrex filter with use of a high-pressure mercury lamp (100 W) under a nitrogen atmosphere at 5 °C for 2 h. After evaporation of the solvent the crude materials were submitted to a short column of alumina to remove the resulting pyridinium bromide. The products eluted with benzene–ether were chromatographed over alumina. The elution with 10% benzene–hexane gave a 26:74 mixture of (*E*)- and (*Z*)-1-bromo-1,2-diphenylpropene. The products eluted with 20% benzene–hexane was assigned to (*E*)-1-methoxy-1,2-diphenylpropene ((*E*)-**5a**) on the basis of spectral data. NMR δ (CCl_4) 2.08 (s, 3 H, CH_3), 3.29 (s, 3 H, OCH_3), 6.82 (s, 5 H, ArH), and 6.88 (s, 5 H, ArH). UV λ_{max} (cyclohexane) 271 nm ($\epsilon \sim 7020$). The product eluted with 40% benzene–hexane was assigned to (*Z*)-1-methoxy-1,2-diphenylpropene ((*Z*)-**5a**) on the basis of spectral data. Mp 53–55 °C. NMR δ (CCl_4) 1.91 (s, 3 H, CH_3), 3.13 (s, 3 H, OCH_3), and 6.90–7.35 (m, 10 H, ArH). UV λ_{max} (cyclohexane) 266 nm ($\epsilon \sim 12000$). (*E*)- and (*Z*)-**5a** were further confirmed by acid hydrolysis to the corresponding ketone. (*E*)- and (*Z*)-**5a** were respectively stirred in a solution of ethanol (5 mL) and concentrated hydrochloric acid (1 mL) at room temperature for 12 h. The product was extracted with ether, and the organic layer was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate. After evaporation of the ether both cases respectively gave the same product, 2-phenylpropiophenone.[19] Elution with benzene gave 9-methoxy-10-methylphenanthrene (**6a**).[3a] The yields of the products, (*Z*)-**5a** (27%), (*E*)-**5a** (32%), and **6a** (22%), were determined from NMR by use of *tert*-butylbenzoic acid as an internal standard.



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