

A NOVEL *ORTHO*-SUBSTITUENT EFFECT ON FORMATION OF VINYL CATIONS
IN THE PHOTOLYSIS OF VINYL BROMIDES

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Introduction of a substituent into *ortho*-position of β -aryl group in a vinyl bromide resulted in the preferential formation of a vinyl cation in the photolysis. It is considered that the steric repulsion of β -aryl groups makes a convenient conformation for an electron transfer from the aromatic ring to the halogen atom in the radical pair.

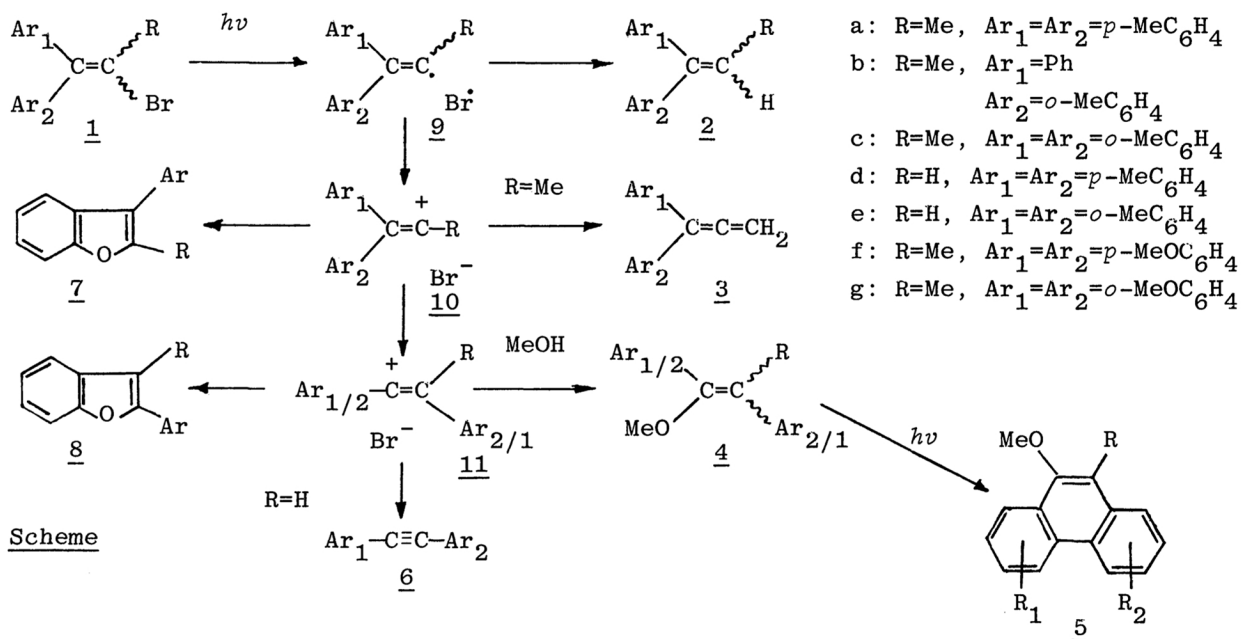
There are some examples that photolysis of vinyl halides gives ionic products as well as radical products.¹⁾ In those papers an electron transfer process in the radical pair has been proposed for the formation of a vinyl cation. Now we report here a curious *ortho*-substituent effect on formation of vinyl cations.

Irradiation of β,β -diarylvinyl bromide 1 (0.01 M) was carried out in methanol containing pyridine (0.012 M) as a buffer with a 100-W high-pressure Hg lamp under N₂ atmosphere. After workup of the reaction mixture the products were separated by a column chromatography on alumina and identified on the basis of the spectral data and chemical behavior. The results are summarized in Table.

As reported in previous papers^{1,7)} the reaction path of each products is explained as follows. The olefin 2 is derived from the vinyl radical 9 which is formed by homolysis of the C-Br bond. The allene 3²⁾ is formed by deprotonation of the vinyl cation 10 which is generated by an electron transfer in 9.³⁾ The vinyl ether 4²⁾ is formed by the nucleophilic attack of methanol on the rearranged vinyl cation 11. The phenanthrene 5²⁾ is obtained by the stilben-like photocyclization of 4. The acetylene 6 is formed by deprotonation of 11. The formation of the benzofurans 7 and 8 is derived from an intramolecular cyclization of 10 and 11, respectively, as discussed previously.⁴⁾ Consequently, radical product is 2 and ionic products are 3, 4, 5, 6, 7, and 8.

As seen from Table, the *ortho*-isomers 1b, 1c, 1e, and 1g afforded ionic products preferentially compared with the corresponding *para*-isomers 1a, 1d, and 1g. This phenomenon is explained as follows. As the result of an introduction of an *ortho*-substituent to the β -aryl groups, the β -aryl groups are twisted from the plane of the ethylene double bond and face to the halogen atom which is formed by homolysis of the C-X bond. This steric factor favors the easiness of an electron transfer between the aromatic ring and the halogen atom, to form a vinyl cation.

Both the absorption wavelength and the extinction coefficient of the *ortho*-substituted vinyl bromides are shorter and smaller than those of the corresponding *para*-isomers.⁵⁾ Therefore, it is reasonable to consider that *ortho*-substituted phenylvinyl halides have an aryl twisted structure⁶⁾ and that the twisted structure makes the electron transfer process in the radical pair favorable.

Table. Photolysis of the vinyl bromide 1 in methanol.

Starting material	Irradiation time / h	Conv. / %	Yield / % ^{a)}						
			<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
<u>1a</u>	3	86	29	16	0	18	-	-	-
<u>1b</u> ^{b)}	2	82	16	17	33	0	-	-	-
<u>1c</u>	3	80	0	18	41 ^{c)}	0	-	-	-
<u>1d</u>	1	74	17	-	22	0	29	-	-
<u>1e</u>	2	91	0 ^{d)}	-	61	0	7	-	-
<u>1f</u> ^{e)}	2	86	19	10	0	36	-	-	-
<u>1g</u> ^{f)}	1.5	93	6	11	0	0	-	27	33

(a) Based on the consumed vinyl bromide 1. Determined by NMR or GC. (b) A ca 1:1 mixture of E- and Z-isomers. (c) Ar₁/2; Ar₁:Ar₂ = 1:10. (d) A trace of 2d was detected by GC. (e) Ref. 7. (f) Ref. 4.

References

- 1) (a) T.Suzuki, T.Sonoda, S.Kobayashi, and H.Taniguchi, *J.Chem.Soc.Chem.Commun.*, 1976, 180. (b) S.A.McNeely and P.J.Kropp, *J.Am.Chem.Soc.*, **98**, 4319(1976). (c) B.Sket and M.Zupan, *J.Chem.Soc.Perkin Trans.I*, **1979**, 175.
- 2) 3a: $\delta(\text{CCl}_4)$ =2.30(s,Me), 5.07(s,CH₂), and 6.92(s,ArH). 3b: $\delta(\text{CCl}_4)$ =2.10(s,Me), 4.95(s,CH₂), and 6.98(bs,ArH). 3c: $\delta(\text{CCl}_4)$ =2.17(s,Me), 4.87(s,CH₂), and 6.95(s,ArH). Acid hydrolysis of 4 gave the corresponding propiophenones and acetophenones, respectively. 5a: picrate, mp.151.5-153.5 °C(from EtOH-benzene).
- 3) T.Kitamura, S.Kobayashi, and H.Taniguchi, *Chem.Lett.*, **1978**, 1223.
- 4) T.Suzuki, T.Kitamura, T.Sonoda, S.Kobayashi, and H.Taniguchi, *J.Org.Chem.*, **46**, 5324(1981).
- 5) $\lambda_{\text{max}}(\log \epsilon)$: 1a(EtOH) 246nm(4.16); 1b(EtOH) 238^{sh}nm(4.01); 1d(EtOH) 240(4.22) and 246nm(4.18); 1e(EtOH) 235^{sh}(4.10) and 247^{sh}nm(4.05); 1f(cyclohexane) 245(4.25) and 270^{sh}nm(4.03); 1g(EtOH) 276(3.77) and 282nm(3.79).
- 6) H.Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press Inc., New York, 1967.
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