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Importance of β Phenyl Group in Ipso Substitution of Arylvinyl Cations

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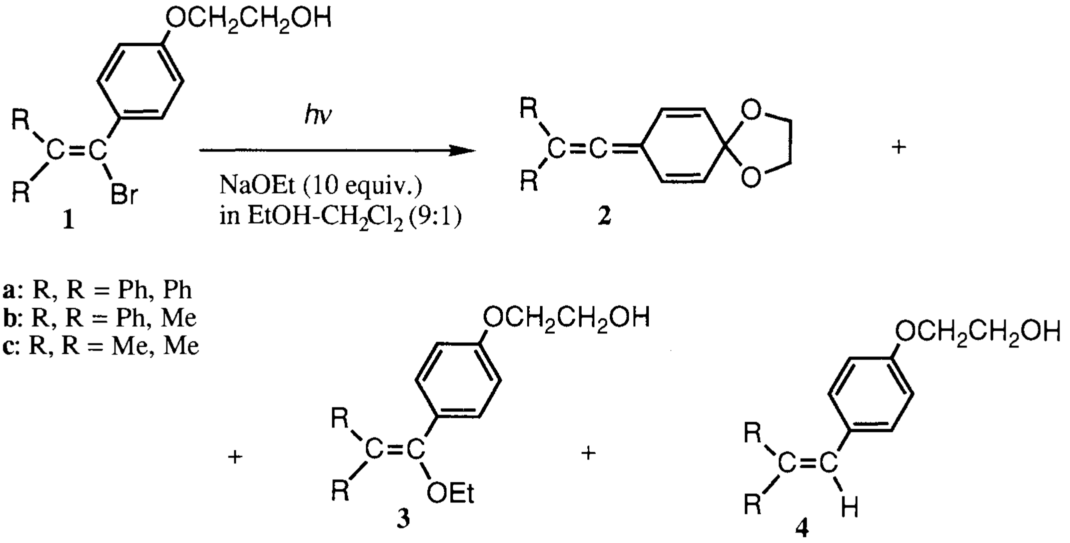
Intramolecular and intermolecular ipso substitutions of arylvinyl cations, i.e., α-[*p*-(2-hydroxyethoxy)phenyl]vinyl cations and α-(*p*-methoxyphenyl)vinyl cations, were studied with respect to the effect of the β substituent and phenyl group as the β substituent was found to exert a significant influence on the ipso substitution.

Ipso substitution (substitution at aromatic ring) of aryl-substituted carbocations has been found in benzylic[1)] and arylvinyl[2)] cations and it has been discussed on several factors affecting the ipso substitution. Especially substituents at the para position of the aryl ring and benzylic substituents of benzylic cations significantly influence charge delocalization which facilitates nucleophilic attack at the aromatic ring. However, little attention has been paid to the substituent of β position. Very recently it has been reported[1a)] that β fluorine atom in CF_3-substituted benzyl cations mainly exerts inductive effect contributing enhancement of charge delocalization. At the outset of this study we were not aware that β phenyl group is important to ipso substitution because there is not large effect of β substituent on vinyl cations[3)] and β phenyl substituent does not contribute the enhancement of the charge delocalization facilitating the ipso attack. However, it was found a drastic decrease of the products derived from ipso substitution when phenyl group at the β position was replaced by methyl group. This paper describes our preliminary studies on β substituent effect of ipso substitution, i.e., importance of β phenyl group.

In order to study the effect of β substituents on arylvinyl cations, the reactions of β-methyl-β-phenylvinyl and β,β-dimethylvinyl cations was examined and compared to that of β,β-diphenylvinyl cations. Intramolecular ipso substitution takes place selectively and is favorable for studying effect of β substituent. Photolysis of 1-bromo-1-[*p*-(2-hydroxyethoxy)phenyl]ethenes (**1**) was conducted by use of a Pyrex-filtered Hg lamp (100 W) in ethanol-dichloromethane (9:1) with NaOEt (10 equiv.) at 3 ^{o}C. The products were 8-



a: R, R = Ph, Ph
b: R, R = Ph, Me
c: R, R = Me, Me

Table 1. Photolysis of Bromides **1** in the Presence of NaOEt

Bromide	Irrad. time/ h	Products, %yield a)			Ratio of ipso adduct to vinylic product, ([**2**] / [**3**])
		2	**3**	**4**	
1a	3	78	trace	- b)	> 99 / 1
1b f)	3	37	39 c, g)	21 d, h)	49 / 51
1c	1 e)	3	49	13	6 / 94

a) Conversions were more than 80%. Yields were determined by ^{1}H NMR (400 MHz) using 1,2-diphenylethene as an internal standard on the basis of the consumed bromide **1** but determined on the basis of the starting bromide **1a** in the case of **1a**. b) Not determined. c) Containing 6% of **5b**. d) Containing 3% of **6b**. e) Without a Pyrex filter. f) E isomer. g) E/Z = 62/38. h) E/Z = 61/39.

vinylidene-1,4-dioxaspiro[4.5]deca-6,9-dienes (**2**),4) 1-ethoxy-1-[*p*-(2-hydroxyethoxy)phenyl]ethenes (**3**), and [*p*-(2-hydroxyethoxy)phenyl]ethenes (**4**). In the case of photolysis of **1b** (R, R = Ph, Me), 3-ethoxy-10-(2-hydroxyethoxy)-9-methylphenanthrenes (**5b**) and 9-(2-hydroxyethoxy)-10-methylphenanthrenes (**6b**) were also formed as the secondary photoproducts. Table 1 indicated a drastic effect of β substituent on formation of ipso adducts **2**. β,β-Diphenyl-substituted bromoethene **1a** is the best system for ipso substitution among the bromoethenes employed. Displacement of phenyl group by methyl group remarkably decreases the formation of ipso adducts **2** and, instead, increases the products **3** derived from vinylic substitution.

The data obtained from intramolecular ipso substitution actually showed significant effect of β substituents.In the case of β-methyl-substituted bromoethenes **1b** and **1c**, however, the increased formation of reduced products **4b** and **4c** might be somewhat troublesome to evaluate the β substituent effect. Moreover, the stability of the ipso adduct **2c** is unclear. Then, we examined ipso substitution under solvolytic conditions which was found by us very recently.5)

Solvolysis of 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene **7a** in EtOH in the presence of NaOEt (10 equiv.) at 120 °C was conducted previously.5) The formation of 1-ethoxy- and 1-bromo-1-(*p*-ethoxyphenyl)-2,2-diphenylethenes **8a** and **9a** clearly indicates that the substitution reaction takes place mainly at the ipso position of the α aryl group. Solvolysis of bromoethenes **7b** and **7c** similarly gave the products derived from ipso and vinylic attacks (Table 2). However, replacement of the β phenyl group by methyl group showed a dramatic change of the ratio of the ipso products to the vinylic products, indicating strongly

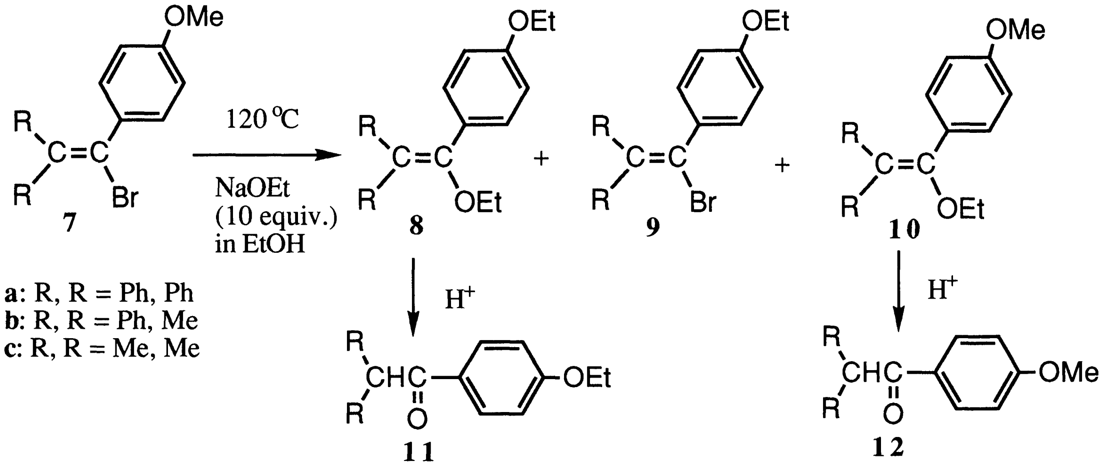


Table 2. Solvolysis of Bromides **7** in EtOH in the Presence of NaOEt

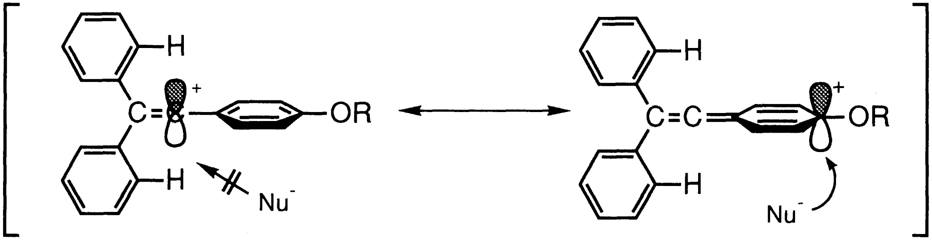
Bromide	Rexn time/ h	Rroducts after acid hydrolysis, %yield a)				Ratio of ipso adducts to vinylic product, {([11] + [9]) / [12]}
		11	**9**	**12**	**7**	
7ab)	65	26	18	15	41	75 / 25
7bc, d)	48	29	0	60	0	33 / 67
7c	16	5	0	62	33	8 / 92

a) Yields were determined by ^{1}H NMR (400 MHz) using hexamethylbenzene as an internal standard after acid hydrolysis. **8b** and **10b** were formed as a mixture of E and Z isomers. b) Ref. 5. c) 1-(*p*-Methoxyphenyl)-2-phenylpropene was also formed in a 17% yield. d) E isomer.

importance of β phenyl group to ipso substitution again.

Both results from intramolecular and intermolecular ipso substitutions show that β,β-diphenyl-substituted vinyl cations are the good systems running ipso substitution and the displacement of phenyl group by methyl group remarkably decreases the ipso attack compared to the vinylic attack.

It is considered that this tendency is attributed to the decreasing steric bulkiness of the β substituent. In the β,β-diphenyl-substituted vinyl cations, a vacant p orbital on the cationic sp carbon lies on the plane of the double bond and very close to the ortho hydrogen atoms of β phenyl groups. Accordingly, β phenyl group sterically hinders the attack of nucleophiles at the vinylic position and expedites the attack at the ipso position because the strong electron-donating alkoxy group delocalizes the charge into the α aryl group and facilitates the attack at the ipso position.



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4) **2a**: Mp 113-115 °C; ^{1}H NMR ($CDCl_3$) δ 4.70 (s, CH_2CH_2), 5.84 (d, J = 10 Hz, =CH), 6.51 (d, J = 10 Hz, =CH), 7.28-7.32 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 213.86 ($C=\underline{C}=C$). **2b**: Mp 96-100 °C; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, Me), 4.09 (s, CH_2CH_2), 5.82 (d, J = 10 Hz, =CH), 6.41 (d, J = 10 Hz, =CH), 7.20-7.38 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 212.49 ($C=\underline{C}=C$). **2c** could not be isolated. ^{1}H NMR ($CDCl_3$) δ 1.74 (s, Me), 3.91 (s, CH_2CH_2), 5.70 (d, J = 10 Hz, =CH), 6.30 (d, J = 10 Hz, =CH).

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