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Ipso Substitution by Alkoxide Ions in Photolysis of Triarylvinyl Halides. Firm Evidence for Intervention of Vinyl Cations

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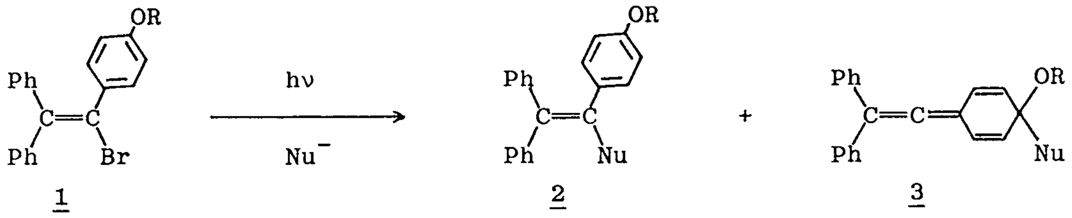
Photolysis of 1-bromo-2,2-bis(p-alkoxyphenyl)-1-phenylethenes in the presence of sodium ethoxide in ethanol gave ipso adducts bearing 1,2-aryl rearranged structure, indicating that ipso substitution proceeds via vinyl cations.

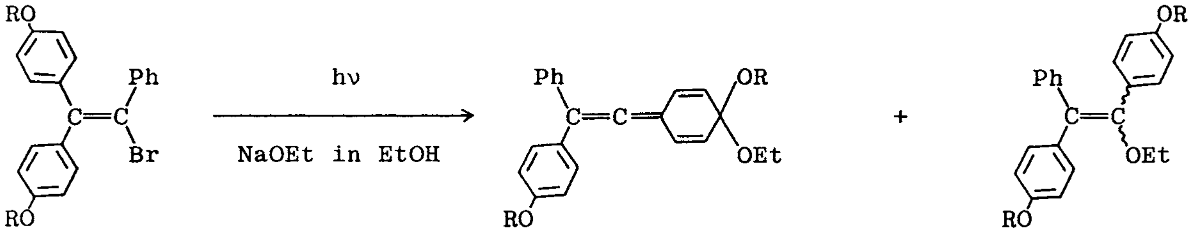
During the course of an investigation on photolysis of arylvinyl halides,[1)] we found that ipso substitution takes place in the case of photolysis of α-(p-alkoxyphenyl)vinyl bromides using some nucleophiles such as cyanide and alkoxide ions.[2)] Especially the reaction of α-(p-alkoxyphenyl)vinyl bromides 1 with an alkoxide ion as a nucleophile resulted in formation of the ipso adducts 3 in good yields.[3)] However, the reaction of the vinyl bromides 1 under solvolytic conditions or under photolytic conditions in the presence of a weak base (amines, for example) gave only vinyl ethers 2 (Nu = OR') but never yielded the ipso adducts 3.



Nu = OR', CN

Accordingly, there is a possibility that use of a strong base, an alkoxide ion, as a nucleophile and a photochemical method cause a direct ipso substitution either by nucleophilic or by S_{RN} reaction$^{4)}$ without forming vinyl cations. Then, in order to elucidate the mechanism for formation of the ipso adducts, we conducted photolysis of α-phenyl-β, β-bis(p-alkoxyphenyl)vinyl bromides. Here we wish to report formation of ipso adducts accompanying 1,2-aryl migration across the double bond as the evidence for a vinyl cation mechanism.

Irradiation of 1-bromo-2,2-bis(p-ethoxyphenyl)-1-phenylethene (4a) in ethanol (0.01 mol/dm^3) in the presence of 10 equiv. of sodium ethoxide was carried out at 0-5 ℃ under nitrogen atmosphere for 4 h by use of a Pyrex-filtered high pressure Hg lamp (100 W). The products were 3,3-diethoxy-6-[2'-(p-ethoxyphenyl)-2'-phenylethenylidene]-1,4-cyclohexadiene (5a) (ipso adduct) (58%) and a mixture of E- and Z-1-ethoxy-1,2-bis(p-ethoxyphenyl)-2-phenylethenes (6a) (20%). Because the ipso adduct 5a was unstable and could not be isolated, it was characterized by ^{1}H and ^{13}C NMR and IR: ^{1}H NMR δ ($CDCl_3$) 1.20 (t, Me), 3.52 (q, CH_2), 5.90 (d, J = 10 Hz, CH=), and 6.51 (d, J = 10 Hz, CH=); ^{13}C NMR δ ($CDCl_3$) 212.17 ($C=\underline{C}=C$); IR 1912 cm^{-1} (C=C=C). The data agree with those of the reported ipso adduct [^{1}H NMR δ ($CDCl_3$) 1.21 (t, Me), 3.52 (q, CH_2), 5.92 (d, J = 10 Hz, CH=), 6.56 (d, J = 10 Hz, CH=); ^{13}C NMR δ (C_6H_6) 213.48 ($C=\underline{C}=C$); IR 1910 cm^{-1} (C=C=C) for 3,3-diethoxy-6-(2,2-diphenylethenylidene)-1,4-cyclohexadiene(3: Nu = OEt,



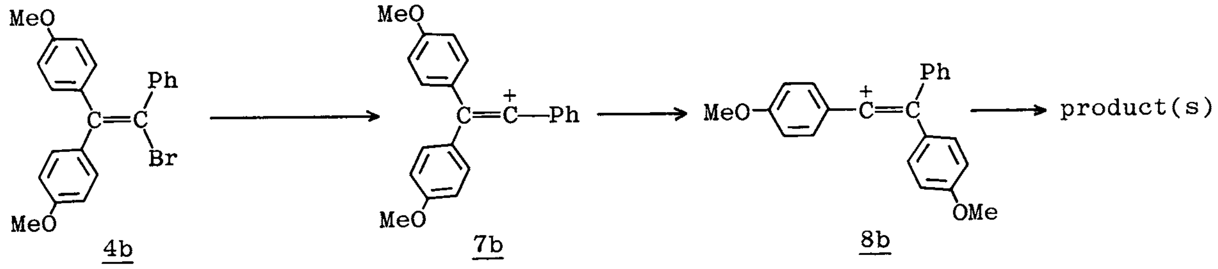
4a: R = Et
4b: R = Me

5a: R = Et
5b: R = Me

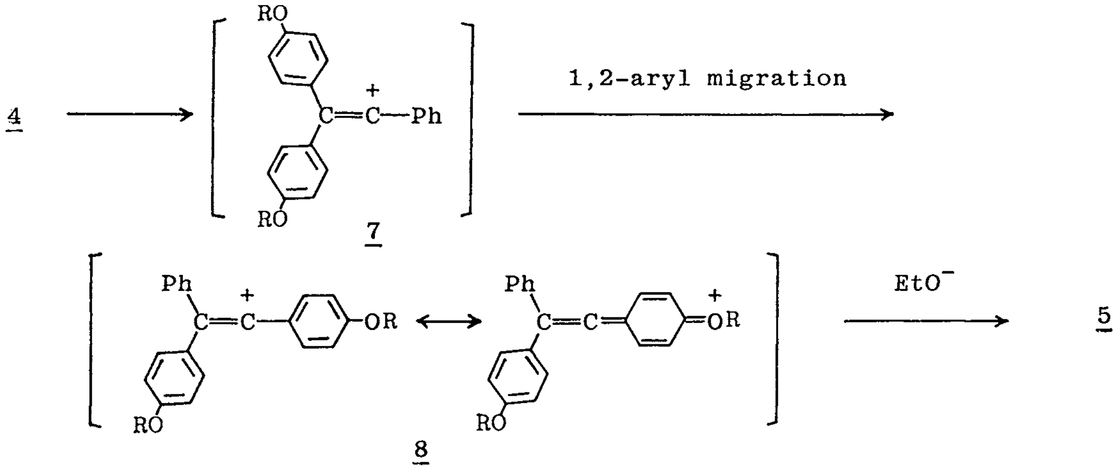
6a: R = Et
6b: R = Me

R = Et)].$^{3)}$ Acid hydrolysis of the reaction mixture with aq. EtOH containing HCl afforded 1,2-bis(p-ethoxyphenyl)-2-phenylethanone as the sole product, indicating that the ipso adduct had the 1,2-aryl rearranged structure. Irradiation of 1-bromo-2,2-bis(p-methoxyphenyl)-1-phenylethene (4b) in ethanol (0.01 mol/dm^3) in the presence of 10 equiv. of sodium ethoxide for 3 h gave, similarly, ipso adduct, 3-ethoxy-3-methoxy-6-(2'-(p-methoxyphenyl)-2'-phenylethenylidene)-1,4-cyclohexadiene (5b), in a 40% yield, together with vinyl ethers 6a$^{5)}$ (49%). The above experiments clearly show that photoreaction of β, β-bis(p-alkoxyphenyl)-α-phenylvinyl bromides 4 gives ipso adducts 5 with the β-aryl rearranged structure. Irradiation of 4b for 0.5 h under the conditions simlar to 3-hr irradiation yielded 5b (35%) and 6b (43%). The ratio [5b]/[6b] is not dependent on the irradiation time. Furthermore, irradiation of 6b in the presence of 10 equiv. of NaOEt in EtOH for 4 h did not afford the ipso adduct 5b but recovered 6b unchanged. These experiments suggest that ipso adduct 5 is not derived from vinyl ether 6.

β-Aryl rearangement in arylvinyl cations has been extensively studied in solvolysis$^{6)}$ and in photolysis.$^{7,8)}$ Rappoport and his coworkers reported that 100% rearrangement of β-aryl group takes place in solvolysis of vinyl bromide 4b.$^{9)}$ We observed the β-(p-methoxyphenyl) migration by laser flash photolysis of 4b.$^{8)}$ A direct attack by ethoxide ion never produces the ipso adduct 5 because the ipso adduct 5 has a β-aryl rearranged structure. The observed 1,2-aryl migration must proceed in vinyl cations.$^{6-8)}$ The fact that in the photolysis of β, β-bis(p-alkoxyphenyl)-α-phenylvinyl bromides 4 the formation of the ipso adduct 5 supports strongly the mechanism involving vinyl cations as below. Thus, irradiation of arylvinyl bromide 4 first generates α-phenylvinyl cation 7, which undergoes 1,2-(p-alkoxyphenyl) migration across the double bond to yield a more stable α-(p-alkoxyphenyl)vinyl cation 8. This vinyl cation 8 is stablized by alkoxyl group on the phenyl ring and the plus charge should delocalize on the aromatic ring. As the result, attack by ethoxide ion$^{10)}$



at the ipso position of the aryl group on vinyl cation 8 leads to formation of 5.



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10) Alkoxide ions can attack at the ipso position, whereas alcohols attack at the vinylic position. See, Ref. 3.

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