# A Novel Spiro Adduct from Intramolecular *ipso* Substitution in the Photolysis of an α-[*p*-(2-Hydroxyalkoxy)phenyl]vinyl Bromide

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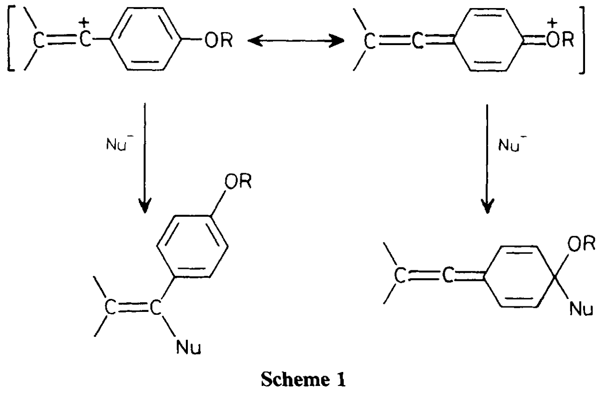
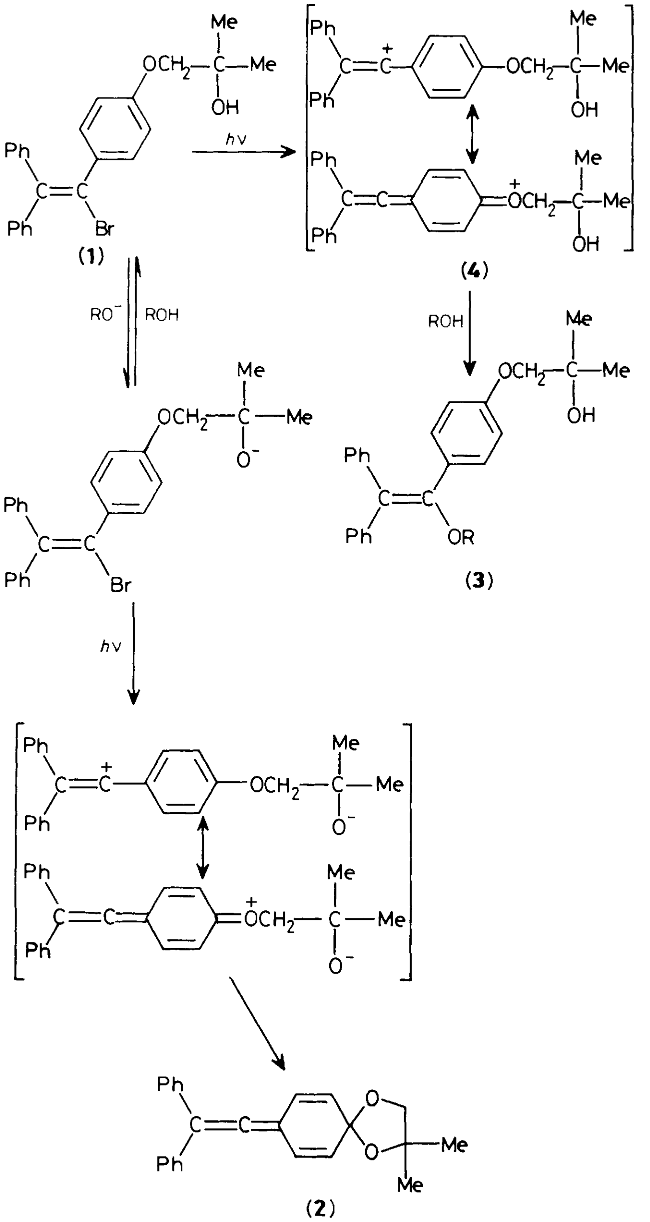
A 1,4-dioxaspiro[4.5]deca-6,9-diene was obtained in high yield by photolysis of 1-bromo-1-[*p*-(2-hydroxy-2-methylpropoxy)phenyl]-2,2-diphenylethene in the presence of sodium 2-propoxide.

Vinyl cations are important intermediates in nucleophilic substitution of vinyl derivatives.[1] Until now, there was no doubt that the nucleophilic substitution of α-arylvinyl cations occurs at the cationic centre of the double bond. However, a strong electron-donating group such as an alkoxy group at the *para* position of the arylvinyl cations delocalizes the positive charge into the aryl ring and is expected to facilitate a hitherto unknown *ipso* substitution. The current development of photochemical formation of carbenium ions involving vinyl cations[2] allows the use of a photochemical technique to study the *ipso* substitution. However, to our knowledge *ipso* substitution has not been observed during the reaction of vinyl cations, except in our previous work[3,4] reporting two reaction paths for nucleophilic substitution, *i.e.*, vinylic and *ipso* attacks in α-(*p*-alkoxyphenyl)vinyl cations. If the nucleophile



Scheme 1



Scheme 2

(Nu) is placed at an intramolecular position suitable for the *ipso* attack, the *ipso* substitution should proceed selectively. We now wish to report exclusive *ipso* attack forming a stable crystalline product.

A solution of 1-bromo-1-[*p*-(2-hydroxy-2-methylpropoxy)-phenyl]-2,2-diphenylethene (**1**) (1 mmol) in propan-2-ol (90 ml)/dichloromethane (10 ml) was irradiated in the presence of sodium isopropoxide (10 mmol) by use of a Pyrex-filtered high-pressure Hg lamp (100 W) for 3 h under $N_2$ atmosphere at 5—10 °C. After removal of the solvent under reduced pressure at 5—10 °C and extraction with ether, crystalline 2,2-dimethyl-8-(2,2-diphenylvinylidene)-1,4-dioxaspiro[4.5]deca-6,9-diene (**2**)†‡ was obtained in 98% yield, which was recrystallized from hexane/dichloromethane to give white crystals, m.p. 141—142 °C.

Dioxaspirodecadiene (**2**) gives a strong peak due to the molecular ion ($M^+$) and a satisfactory elemental analysis (C,H). The i.r. spectrum shows a characteristic absorption at 1912 $cm^{-1}$ due to the allenic bond. The $^1H$ and $^{13}C$ n.m.r. spectra are consistent with the proposed structure. In particular, characteristic alkenic protons [δ 5.88 (d, *J* 10 Hz) and δ 6.49 (d, *J* 10 Hz), AB system] are observed in the $^1H$ n.m.r. spectrum with the allenic carbon observed at δ 214 in the $^{13}C$ n.m.r. spectrum. Dioxaspirodecadiene (**2**) is stable under neutral or basic conditions. However, (**2**) decomposed slowly in methanol or ethanol to afford the corresponding vinyl ether (**3**). The half-life, $t_{1/2}$, of the methanolysis was approximately 60 h at 40 °C.

On the other hand, irradiation of (**1**) with pyridine (10 mol equiv.) in alcohols (MeOH, EtOH, or $Pr^iOH$) did not afford (**2**) at all but yielded 1-alkoxy-1-[*p*-(2-hydroxy-2-methylpropoxy)phenyl]-2,2-diphenylethene (**3**). This result suggests that the terminal hydroxy group cannot attack the *ipso* position of the resulting vinyl cation (**4**). In other words, to achieve the *ipso* substitution, the terminal hydroxy group (–OH) must ionize to give the oxide ion ($-O^-$) on addition of strong base. Accordingly, the dissociation of the terminal hydroxy group is considered as the key process during the *ipso* substitution. The photolysis of (**1**) in the presence of NaOMe or NaOEt, which are less basic than $NaOPr^i$,[5] resulted in the formation of (**2**) and (**3**).

Formation of spiro adduct (**2**) provides firm evidence for the intramolecular *ipso* attack. In addition to the well known vinylic substitution,[1] this new type of reaction (*ipso* substitution) becomes a significant process when a stabilized arylvinyl cation encounters a suitable strong nucleophile.

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† *Spectral data* for (**2**): $^1H$ n.m.r. ($CDCl_3$, 60 MHz) δ 1.39 (s, 6H, Me), 3.86 (s, 2H, $CH_2$), 5.88 (d, *J* 10 Hz, 2H, =CH), 6.49 (d, *J* 10 Hz, 2H, =CH), and 7.32 (br. s, 10H, ArH); $^{13}C$ n.m.r. ($C_6D_6$, 400 MHz) δ 26.93, 75.38, 79.33, 101.84, 102.81, 113.19, 124.79, 128.88, 129.10, 129.13, 129.45, 135.94, 213.95; i.r. (KBr) 1912 (m, C=C=C), 1650 (m, C=C), 1598 $cm^{-1}$ (m, aromatic C=C); *m/z* (rel %) 342 ($M^+$, 47), 327 ($M^+$ – Me, 59), 312 ($M^+$ – 2 × Me, 19), 284 ($M^+$ – 58, 63), 272 ($Ph_2C{=}CHPhOH$, 59), 270 ($Ph_2C{=}C{=}C_6H_4{=}O$, 94), 254 (100), 241 (97).

‡ However, the reaction of (**1**) at room temp. for 12 h in the absence of irradiation resulted in recovery of (**1**), unreacted.