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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 cations² 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 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 N₂ 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) \dagger 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 ¹³C 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 ¹³C 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-methyl-propoxy)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 NaOPrⁱ,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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References

Me

Me

Me

- 1 P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, 'Vinyl Cations,' Academic Press, New York, 1979; Z. Rappoport, in 'Reactive Intermediates,' ed. R. A. Abramovitch, vol. 3, Plenum, New York, 1983.
- 2 T. Kitamura, S. Kobayashi, and H. Taniguchi, J. Am. Chem. Soc., 1986, 108, 2641 and references cited therein.
- 3 T. Kitamura, T. Kabashima, S. Kobayashi, and H. Taniguchi, *Chem. Lett.*, 1988, 1951; T. Kitamura, T. Kabashima, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, 1988, **29**, 6141.
- 4 T. Kitamura, M. Murakami, S. Kobayashi, and H. Taniguchi, Tetrahedron Lett., 1986, 27, 3885.
- 5 W. E. McEwen, J. Am. Chem. Soc., 1936, 58, 1124.

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

[†] Spectral data for (2): ¹H n.m.r. (CDCl₃, 60 MHz) δ 1.39 (s, 6H, Me), 3.86 (s, 2H, CH₂), 5.88 (d, J 10 Hz, 2H, =CH), 6.49 (d, J 10 Hz, 2H, =CH), and 7.32 (br. s, 10H, ArH); ¹³C n.m.r. (C₆D₆, 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); m/z (rel %) 342 (M⁺, 47), 327 (M⁺ - Me, 59), 312 (M⁺ - 2 × Me, 19), 284 (M⁺ - 58, 63), 272 (Ph₂C=CHPhOH, 59), 270 (Ph₂C=C=C₆H₄=O, 94), 254 (100), 241 (97).