

Evidence of a Spiro[2.5]octa-1,4,7-trien-6-one Intermediate in the Solvolysis of β -(*p*-Oxidophenylene)vinyl Bromides

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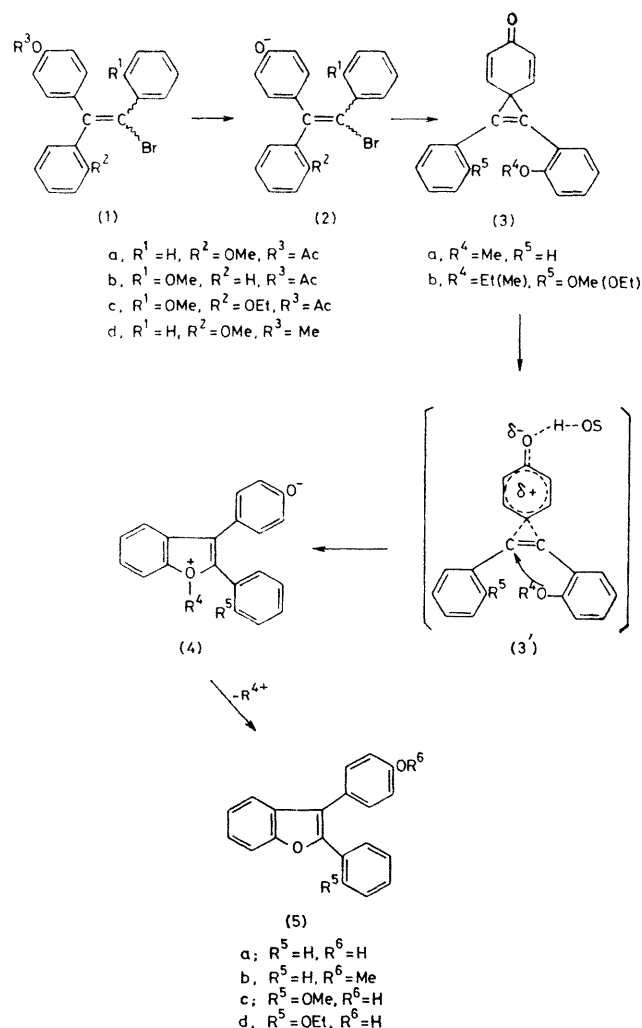
Summary The exclusive formation of 3-(*p*-hydroxyphenyl)-2-phenylbenzofuran from the solvolysis of both 2-(*p*-acetoxyphenyl)-2-(*o*-methoxyphenyl)-1- and 2-(*p*-acetoxyphenyl)-1-(*o*-methoxyphenyl)-2-phenyl vinyl bromide and the formation of a 1:1 mixture of 3-(*p*-hydroxyphenyl)-2-(*o*-methoxyphenyl)- and 2-(*o*-ethoxyphenyl)-3-(*p*-hydroxyphenyl)-benzofuran from 2-(*p*-acetoxyphenyl)-2-(*o*-ethoxyphenyl)-1-(*o*-methoxyphenyl)vinyl bromide under alkaline conditions provide firm evidence for the

presence of the title compound as the precursor of benzofurans of this type

ALTHOUGH spiro[2.5]octa-4,7-dien-6-one has been suggested as the solvolysis intermediate of β -(*p*-oxidophenylene)ethyl bromide,¹ solvolysis of the corresponding vinyl derivatives has never been studied. We report evidence of a spiro[2.5]octa-1,4,7-trien-6-one intermediate in the solvolysis of β -(*p*-oxidophenylene)vinyl bromide, namely its trapping

intramolecularly with an alkoxy-group located at a suitable position.

Heating of *Z*-2-(*p*-acetoxyphenyl)-2-(*o*-methoxyphenyl)-1-phenylvinyl bromide (**1a**) was carried out in 50% aqueous ethanol containing 10 mol. equiv. of sodium hydroxide and 5 mol. equiv. of thiophenol† at 130 °C for 13 h in a sealed tube and crystals, m.p. 151–153 °C, isolated. The ¹H n.m.r. spectrum of the obtained product did not show any peak in the region of methoxy-protons. *Z*-2-(*p*-Acetoxyphenyl)-1-(*o*-methoxyphenyl)-2-phenylvinyl bromide (**1b**), the isomer of (**1a**), was similarly heated at 130 °C for 2 h. The ¹H n.m.r. spectrum of its product was identical with that of the product of (**1a**) and also similar crystals were obtained. The same result was attained from the solvolysis of *E*-(**1b**). The structure of the crystals could be assigned as



SCHEME

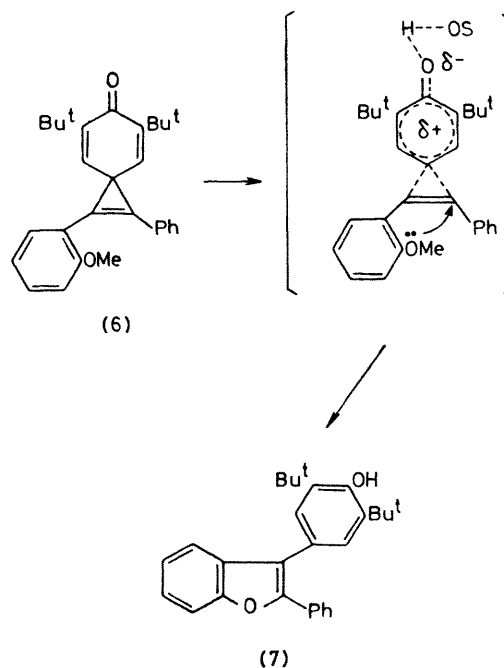
† Thiophenol is used as a trapping reagent for R^{4+} (T. Sonoda, S. Kobayashi, and H. Taniguchi, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2560). The solvolytic reaction of (**1a**) without thiophenol gave the benzofuran (**5a**) (>90 %) as a main product and small amounts of (**1d**) and (**5b**) which are the corresponding methylated compounds of (**2a**) and (**5a**).

‡ (**2a**), $t_{1/2}$ (50% EtOH) 6.7 h at 110 °C, (**2b**), $t_{1/2}$ (50% EtOH) 0.42 h at 80 °C, preliminary results. 2,2-Bis(*p*-methoxyphenyl)-1-phenylvinyl bromide, $t_{1/2}$ (60% EtOH) 42 h at 140 °C (Z. Rappoport and Y. Houminer, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1506) and 1,2-bis(*p*-methoxyphenyl)-1-phenylvinyl bromide (*E*), $t_{1/2}$ (80% EtOH) 0.76 h at 120 °C (Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, 1975, **97**, 836).

¹ R. Baird and S. Winstein, *J. Am. Chem. Soc.*, 1963, **85**, 567.

3-(*p*-hydroxyphenyl)-2-phenylbenzofuran (**5a**), confirmed by methylation to give 3-(*p*-methoxyphenyl)-2-phenylbenzofuran (**5b**), m.p. 87–89 °C, which was identified by a mixed melting point determination with an authentic sample. The ¹H n.m.r. spectra indicated that the formation of (**5a**) was quantitative in all cases. Similar solvolysis of *Z*-2-(*p*-acetoxyphenyl)-2-(*o*-ethoxyphenyl)-1-(*o*-methoxyphenyl)vinyl bromide (**1c**) gave a 1:1 mixture of 2-(*o*-ethoxyphenyl)- and 2-(*o*-methoxyphenyl)-3-(*p*-hydroxyphenyl)benzofuran, (**5c**) and (**5d**).

Hence, the following reaction pathway is suggested (Scheme). First, easy removal of the acetoxy-group of (**1**) under the above reaction conditions gave the corresponding phenolates (**2**). The negatively charged vinyl bromides were solvolysed more easily than is usual for triarylvinyl bromides.‡ Exclusive formation of (**5a**) from (**1a**) and (**1b**) and the formation of both (**5c**) and (**5d**) from (**1c**) suggest that there is a common precursor in which intramolecular nucleophilic attack of the alkoxy-group gives (**5**). The common precursor should be the spiro[2.5]octa-1,4,7-trien-6-one (**3**).



Further evidence of the presence of (**3**) is that treatment of 5,7-di-*t*-butyl-1-(*o*-methoxyphenyl)-2-phenylspiro[2.5]octa-1,4,7-trien-6-one (**6**) with 90% aqueous ethanol containing sodium hydroxide gave exclusively, 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)-2-phenylbenzofuran (**7**).

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