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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-(pacetoxyphenyl)-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-(phydroxyphenyl)-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

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-(oethoxyphenyl)- 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-tbutyl-4'-hydroxyphenyl)-2-phenylbenzofuran (7).

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† Thiophenol is used as a trapping reagent for \mathbb{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).

 \ddagger (2a), $t_{\frac{1}{2}}$ (50% EtOH) 6·7 h at 110 °C, (2b), $t_{\frac{1}{2}}$ (50% EtOH) 0·42 h at 80 °C, preliminary results. 2,2-Bis(*p*-methoxyphenyl)-1-phenylvinyl bromide, $t_{\frac{1}{2}}$ (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), $t_{\frac{1}{2}}$ (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.