

Flash-vacuum Thermolysis of Phenyl-*p*-benzoquinone

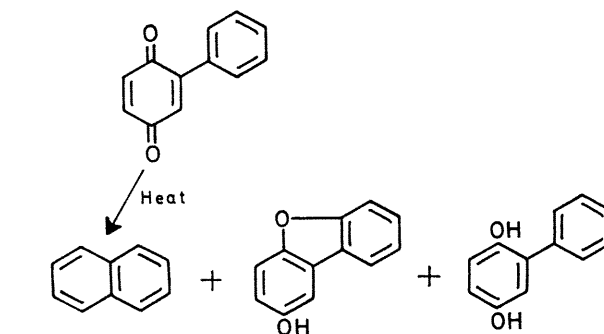
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Summary Flash-vacuum thermolysis of phenyl-*p*-benzoquinone yields naphthalene, 2-hydroxydibenzofuran, and phenyl-1,4-hydroquinone, the formation of naphthalene can be visualised as an intramolecular trapping of either a butadiene diradical, cyclobutadiene, or tetrahedrane by the phenyl ring

RECENTLY we studied photochemical reactions of some aryl-*p*-benzoquinones in solution^{1,2} and in the solid state.² The major reaction was invariably† a photocyclisation to a 2-hydroxydibenzofuran sometimes accompanied by photo-reduction to the corresponding aryl-1,4-hydroquinone. It was of interest to know whether these products could also be obtained under strictly thermal conditions.

Phenyl-*p*-benzoquinone was flash thermolysed *in vacuo* at 800 °C. Tlc showed the presence of three major products in addition to starting material: naphthalene

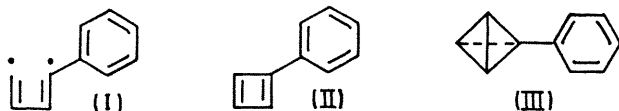


(54%), ‡ 2-hydroxydibenzofuran, m p 136—137° (8%), and phenyl-1,4-hydroquinone (*ca* 8%). Two of the product types formed by the thermolysis are thus identical with

† Except in aromatic solvents, where photodimerisation is the predominant reaction at least in the example studied^{1,2}

‡ Yields were determined by glc and are expressed in mol % based on consumed starting material (conversion of phenyl-*p*-benzoquinone amounted to 60%)

those formed photochemically;² the hydroquinone formation is not considered significant.



Naphthalene can be thought to arise following the loss of two CO molecules from phenyl-*p*-benzoquinone *via* an intramolecular trapping[§] of either a butadiene diradical (I) cyclobutadiene (II), or tetrahedrane (III) by the phenyl

ring. This process is reminiscent of the stepwise loss of CO molecules in the mass spectra of *p*-benzoquinones^{4,5,¶} leading to the formation of $C_4R_4^+$ ions, which have been suggested⁵ to represent substituted tetrahedrane rather than substituted cyclobutadiene species.

We have observed a similar behaviour for several substituted phenyl-*p*-benzoquinones. Since various substituted phenyl-*p*-benzoquinones are readily accessible,⁶ their relatively clean thermolysis provides a useful method for the study of processes which involve cyclobutadiene and/or tetrahedrane intermediates.^{3,7-10}

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§ Trapping certainly is the appropriate description since species (II) and (III) would have given acetylene and/or vinylacetylene⁹ were it not for the presence of the phenyl substituent.

¶ The mass spectrum of phenyl-*p*-benzoquinone (parent ion m/e 184) also showed fragment ions m/e 156 ($M - CO$), and m/e 128 ($M - 2CO$).

¹ H. J. Hageman and W. G. B. Huysmans, *Chem. Comm.*, 1969, 837.

² H. J. Hageman, to be published.

³ Cf. P. B. Shevlin, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 406.

⁴ J. H. Bowie, D. W. Cameron, R. G. F. Giles, and D. H. Williams, *J. Chem. Soc. (B)*, 1966, 335.

⁵ T. A. Elwood, and M. M. Bursey, *Org. Mass Spectrometry*, 1968, **1**, 537.

⁶ Cf. G. A. Reynolds and J. A. Van Allen, *Org. Synth.*, 1963, Coll. Vol. IV, 15.

⁷ E. K. G. Schmidt, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 3240 and references therein.

⁸ J. F. W. McOmie, and B. K. Bullimore, *Chem. Comm.*, 1965, 63.

⁹ E. McNelis, *J. Org. Chem.*, 1965, **30**, 4324.

¹⁰ T. Hosokawa, and I. Moritani, *Bull. Chem. Soc. Japan*, 1970, **43**, 959.