

## Flash Thermolysis: the Formation of Aldehydes from Anisole Derivatives

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**Summary** The thermolysis of several anisoles gives benzaldehyde: the mechanism is discussed.

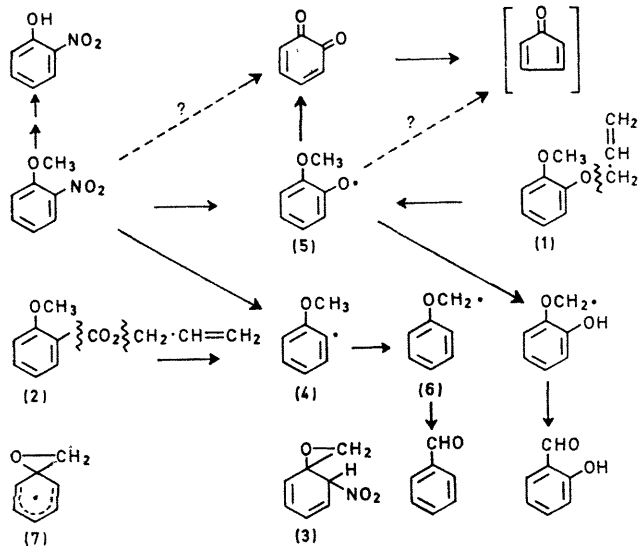
THERMOLYSIS<sup>1</sup> of *o*-nitroanisole at 900° (80% conversion) gives benzaldehyde in 40 mol % yield as the major product. Other identified compounds† from this reaction (mol % yields in parentheses) are salicylaldehyde (5), *o*-nitrophenol (5), phenol (2·5), and cyclopentadienone (as the dimer, 2).‡

That the aldehyde group is generated at the position originally occupied by the methoxy-group was clearly shown by thermolysis of 4-methyl-2-nitroanisole which gave *p*-tolualdehyde (37) and 2-hydroxy-4-methylbenzaldehyde (5). In addition, the thermolysis of the deuteriated (OCD<sub>3</sub>) ether gave *p*-tolualdehyde totally and specifically labelled at the aldehyde carbon and at the *ortho*-position to it.

† Products were divided into phenols and neutral compounds, separated by t.l.c., and each component identified spectroscopically and also by conversion into appropriate derivatives. Yields were determined by <sup>1</sup>H n.m.r. spectroscopy.

‡ F. P. Lossing (N.R.C., Ottawa) has informed us that he has observed the thermolytic formation of benzaldehyde from *o*-nitroanisole and identified the product by direct thermolysis into the mass spectrometer. (O. A. Mamer, R. J. Kominar, and F. P. Lossing, *Org. Mass Spectrometry*, in the press). He has also detected a species said to be methylenedioxybenzene. We have found no trace of this substance (an isomer of salicylaldehyde) which we have shown to be stable under the conditions of our experiments. The reason for this dichotomy is not yet clear. We thank Dr. Lossing most cordially for his helpfulness in an area he has pioneered.

Thermolysis of the allyl ether (1) gave salicylaldehyde (40) whilst the allyl ester (2) gave benzaldehyde (10). Hence the generation of an aldehyde function from a methoxy-group is not uniquely dependent on the presence



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of an *ortho*-nitro-substituent, but rather on a moiety that produces a radical within reacting distance of the methoxy-group.

These results may be rationalized as shown in the Scheme, [although a cyclic non-radical mechanism proceeding through a species such as (3) may be invoked to explain the formation of benzaldehyde from *o*-nitroanisole<sup>2</sup>]. If it be accepted, as has already been suggested,<sup>3</sup> that thermolysis of an aromatic nitro-group may give a phenyl radical (by direct loss of NO<sub>2</sub>) or a phenoxy-radical (*via* a nitrite), then the formation of (4) and (5) is reasonable. Analogy is also available for the thermolytic conversion of catechol derivatives into cyclopentadienone, and of *o*-quinone into the same substance,<sup>4</sup> and for the radical shift.<sup>5</sup>

The mechanism was tested as follows. Both postulated intermediates were generated by alternative routes, (5) from the allyl ether (1)<sup>6</sup> and (4) from the allyl ester (2).<sup>7</sup> In both cases the required product was obtained. These results are compatible with, but do not prove, the suggested mechanism.

No details are yet available concerning the mode of conversion of the phenoxy radical (6) into the aldehyde, but a spiranic oxiran (7) seems likely to be involved. The rearrangement under our present conditions must be rapid since no anisole is formed. In addition, no benzyl alcohol could be detected.

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<sup>1</sup> The thermolyses were carried out at the temperature indicated at a pressure of 10  $\mu$ m Hg (calculated contact time *ca.* 1 m s). For a description of the apparatus see, J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Canad. J. Chem.*, in the press. See also, E. Hedaya, *Accounts Chem. Res.*, 1969, 2, 367; P. de Mayo and D. L. Verdun, *J. Amer. Chem. Soc.*, 1970, 92.

<sup>2</sup> A cyclic mechanism has been suggested for the thermally induced conversion of nitrostyrenes into aromatic carbonyl compounds: T. H. Kinstle and J. G. Stam, *J. Org. Chem.*, 1970, 35, 1771.

<sup>3</sup> E. K. Fields and S. Meyerson, *J. Org. Chem.*, 1970, 34, 62.

<sup>4</sup> D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Letters*, 1967, 271.

<sup>5</sup> M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Chem. Comm.*, 1965, 609.

<sup>6</sup> The formation of phenoxy-radicals from the thermolysis of allyl ethers has been reported: E. Hedaya and D. McNeil, *J. Amer. Chem. Soc.*, 1967, 89, 4213.

<sup>7</sup> A parallel fission has been described in the formation of phenyl radicals in the thermolysis of benzyl benzoate: M. Szwarc and W. J. Taylor, *J. Chem. Phys.*, 1953, 21, 1746.