

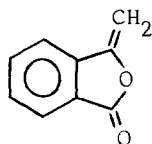
FLASH-THERMOLYSIS OF METHYLENEPHTHALIDE AND 3-METHYLENE-2-COUMARANONE

by R. Bloch and P. Orvane

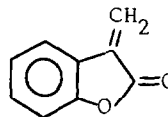
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Summary. The synthesis and flash-thermolysis of methylenephtalide 1 and 3-methylene-2-coumaranone 2 are reported. At high temperatures ($\geq 1000^\circ\text{C}$) these two isomeric lactones do not extrude CO_2 but give rise to new clean thermal rearrangements.

Methylenebenzocyclopropene is a very interesting simple molecule but, to our knowledge, no derivative of this compound has been described so far. Simple molecular orbital calculations indicate that methylenebenzocyclopropene should be more stable and less polymerisable than methylenecyclopropene (1). However, due to the high strain energy associated with the ring system, methylenebenzocyclopropene must be a very reactive species and flash thermolysis appears to be a good technique for the preparation of such a molecule (2). We wish to report the new thermal rearrangements observed during an approach to methylenebenzocyclopropene by flash thermolysis (3) of methylenephtalide 1 and 3-methylene-2-coumaranone 2 (4).

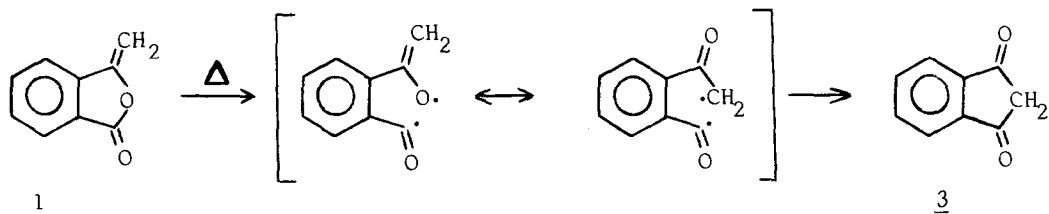


1



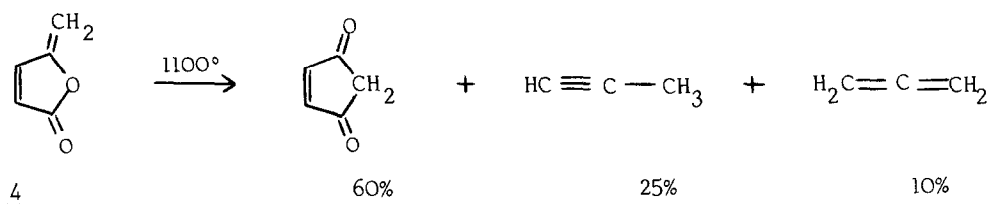
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Flash thermolysis (5) of methylenephtalide 1 (6) was carried out at different temperatures ; the starting material was entirely recovered up to 900°C . At higher temperatures a new unique compound was formed but the degree of conversion was still low ($\sim 50\%$ at 1100°C). The new product appeared from its spectra to be 1,3-indanedione 3 and this was confirmed by direct comparison (IR, ^1H NMR, Mass) with an authentic sample. A plausible mechanism for the rearrangement 1 \longrightarrow 3 is given in scheme 1.



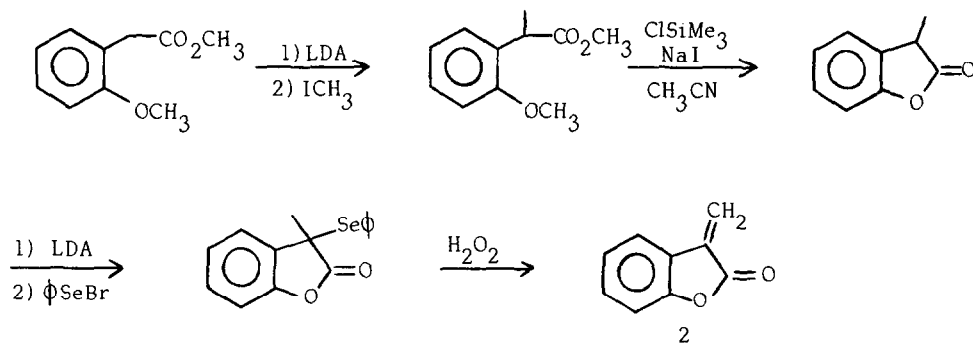
Scheme 1

In contrast to the thermolysis of phthalide where the benzyl-oxygen cleavage is the main process (7), the acyl-oxygen rupture, giving a biradical stabilised by allylic resonance, is the only pathway observed here. Recombination of the biradical leads to 3 without any decarbonylation. Related photochemical rearrangements have been reported, but generally the inverse reaction (1,3-dione \longrightarrow alkylidene lactone) is observed (8). The generality of this thermal rearrangement of methylene butenolides was shown by the thermolysis of protoanemonin 4 (9) leading mainly to cyclopentene-1,3-dione.



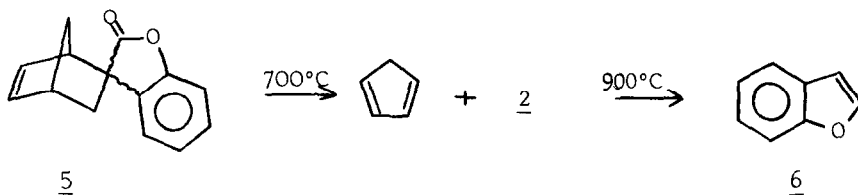
The formation of propyne can be explained by two successive decarbonylations: the first one affords cyclobutenone which is thermally opened into vinylketene (10); then, under the reaction conditions, vinylketene undergoes the second decarbonylation, giving rise to vinylcarbene easily rearranged to propyne (11).

3-Methylene-2-coumaranone 2, an isomer of methylenephthalide, gives entirely different thermolysis products and its synthesis and thermal behaviour are reported below. At least two unsuccessful attempts to synthesize the methylene lactone 2 from 2-coumaranone have been described in the literature (12), the difficulties arising from the inability of the authors to substitute the 3-position of 2-coumaranone via the enolate: even deuteration could not be achieved (12b). We found that the use of lithium-diisopropylamide at -10°C allows the formation of the lithium enolate of 2-coumaranone, which undergoes methylation with methyl iodide in the presence of HMPA; however in these conditions dialkylation preponderates over monoalkylation (ratio 8 : 2) and the compound 2 was thus prepared following scheme 2.



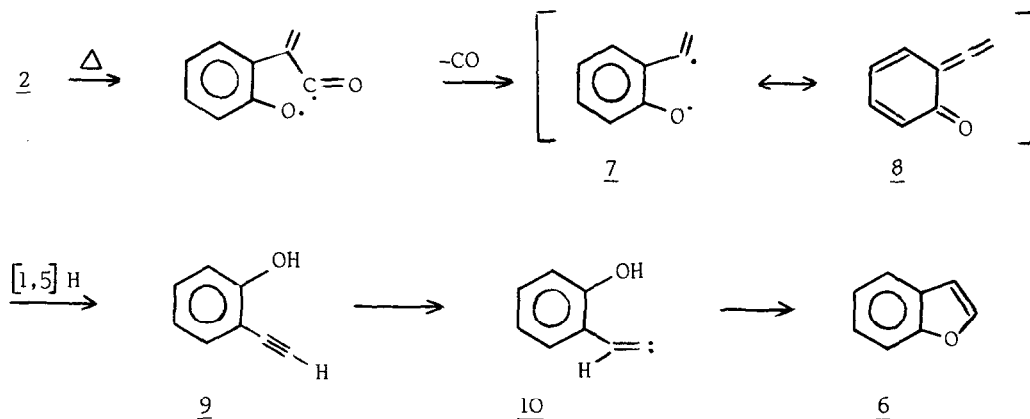
Scheme 2

The lactone 2, stable for a few days in solution, polymerises quickly in the pure state and was purified and kept as its adducts 5 (two isomers) with cyclopentadiene. Flash thermolysis at 700°C of the adducts 5 regenerates cyclopentadiene and the lactone 2 which, at 900°C, decarbonylates to give a new product identified to benzofuran 6 by comparison with an authentic sample. The conversion 2 \rightarrow 6 is quantitative at 1000°C.



The formation of benzofuran 6 from the lactone 2 is rationalized in scheme

3.



Scheme 3

Rupture of the acyl-oxygen bond followed by loss of CO gives, as in the case of 2-coumaranone (7), the biradical 7, a mesomeric form of the allenyl ketone 8 (13). Under the thermolysis conditions there is no recombination of the biradical 7 but rather a [1.5] hydrogen shift leading to 2-hydroxyphenylacetylene 9, which equilibrates with the methylenecarbene 10 (14). The formation of benzofuran arises from the trapping of the carbene function of 10 by insertion into the o-hydroxy group. A support for this scheme was given by the total conversion of 2-hydroxyphenylacetylene into benzofuran when heated at 800°C.

REFERENCES AND NOTES

- 1) The calculations were performed with the help of C. Minot.
- 2) Benzocyclopropene, despite its high reactivity versus electrophilic and nucleophilic reagents, exhibits a remarkable thermal stability. See W.E. Billups, Accounts Chem. Res., **11**, 245 (1978).
- 3) For a recent review on flash thermolysis see R.F.C. Brown, "Pyrolytic methods in organic chemistry", Academic Press Inc., New York, 1980.
- 4) High vacuum thermolysis of phthalide and 2-coumaranone are well documented, see a) C. Wentrup and P. Muller, Tetrahedron Lett., 2915 (1973); b) U.E. Wiersum and T. Nieuwenhuis, Tetrahedron Lett., 2581 (1973).
- 5) The apparatus used is analogous to the one described by J.F. King, P. de Mayo, C.L. Mac Intosh, K. Piers and D.J.H. Smith, Can. J. Chem., **48**, 3704 (1970).
- 6) Prepared according to S.V. Vinagrova, Zh. Prikl. Khim. (Leningrad), **44**, 1389 (1971).
- 7) C. Wentrup, Tetrahedron Lett., 2919 (1973).
- 8) a) J. Rigaudy and P. Derible, Bull. Soc. Chim. Fr., 3047 (1965); b) H. Nozaki, Z. Yamaguti and R. Noyori, Tetrahedron Lett., 37 (1965).
- 9) Synthesized according to C. Grundmann and E. Kober, J. Amer. Chem. Soc., **77**, 2332 (1955).
- 10) J.L. Ripoll, A. Rouessac and F. Rouessac, Tetrahedron, **34**, 19 (1978).
- 11) R.D. Streeper and P.D. Gardner, Tetrahedron Lett., 767 (1973).
- 12) a) J. Martin, P.C. Watts and F. Johnson, J.C.S. Chem. Comm., 27 (1970); b) A.D. Harmon and C.R. Hutchinson, J. Org. Chem., **40**, 3474 (1975).
- 13) As this work was in progress, a similar rearrangement was observed by thermolysis of furan-2 (3H)-ones: in this case the allenyl ketones formed were stable enough to be isolated and identified; no furans have been detected; H.M. Besterman, R. Harder, H.W. Winter and C. Wentrup, Angew. Chem. Int. Ed., **19**, 564 (1980).
- 14) The equilibrium arylacetylenes \rightleftharpoons arylmethylene-carbenes at high temperatures has been detected by ^{13}C labelling experiments by R.F.C. Brown, F.W. Eastwood, K.J. Harrington and G.L. Mc Mullen, Aust. J. Chem., **27**, 2393 (1974). Such a methylenecarbene is the intermediate proposed for the conversion:

o-Tolylacetylene $\xrightarrow{720^\circ\text{C}}$ Indene.

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