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AN UNUSUAL THERMAL DECOMPOSITION OF A FORMAL OXIRENE-DIENE ADDUCT

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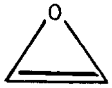
Flash thermolysis of benzo-3,8-dioxatricyclo[3.2.1.$0^{2,4}$]-6-octene gave a dialdehyde and indene.

Our interest in oxacyclopropene (oxirene), 1, led us to investigate the thermolysis of various formal Diels-Alder adducts of 1 and arenes or dienes, in the hope of observing the reverse Diels-Alder reaction.[1] Since the formal ethene-isobenzofuran adduct 2 has been reported to fragment quantitatively to ethene and isobenzofuran on flash thermolysis,[2] we investigated the flash thermolysis of the formal oxirene-isobenzofuran adduct 3.[3] We have found that 3, rather than undergoing a reverse Diels-Alder reaction to give 1 and isobenzofuran, exhibits an unusual fragmentation process to yield, besides the dialdehyde 4, indene (5).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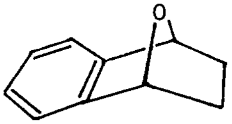
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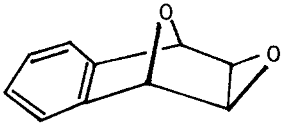

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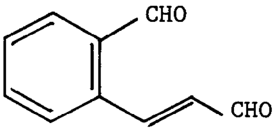

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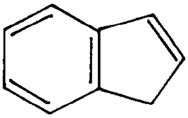
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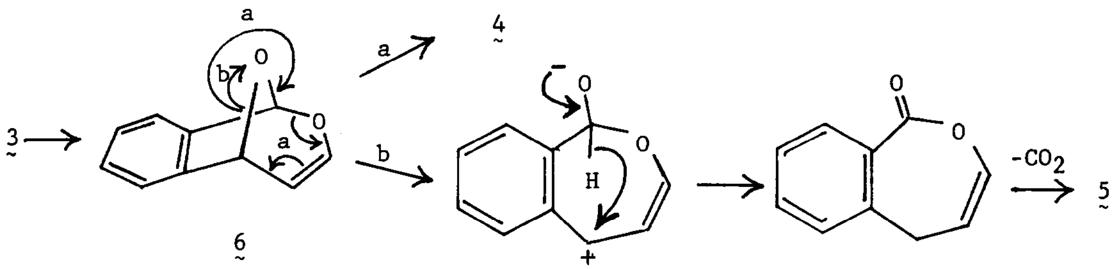
When the epoxide 3 was sublimed through a quartz tube at 600°/ca. 10^{-3} torr, a thermolysate was obtained from which 4 and 5 (ca. 50% yield of each) were isolated by preparative TLC.

The ^{1}H NMR spectrum of the crude mixture showed it to be essentially only 4 and 5, and GLC and TLC revealed the presence of essentially only two components. IR, ^{1}H NMR, and mass spectrometry indicated the structure of the more polar TLC component to be 4, and this was confirmed by direct comparison (IR, ^{1}H NMR, and mixture m.p.) with an authentic sample synthesized from the corresponding diacid (Aldrich Chemical Co.) by $LiAlH_4$-$AlCl_3$ reduction to the diol[4] and oxidation of this to 4 with pyridinium chlorochromate.[5] Dialdehyde 4, m.p. 57-58°, shows the following spectra: IR, λmax (CCl_4) 5.96, 5.98 μm; ^{1}H NMR, δ($CDCl_3$) 6.52 (d of d, J = 8 and 16 Hz ; 1 H), 7.0-8.0 (m, spike at 7.58; 4H), 8.40 (d, J = 16Hz; 1H), 9.58 (d, = 8Hz; 1H), 10.03 (s; 1H).

The less polar TLC component appeared from its spectra to be indene, 5, and this was confirmed by direct comparison (IR, ^{1}H NMR, GLC coinjection) with an authentic sample. The formation of indene is of particular interest. This represents loss of the elements of CO_2, and since extrusion of atomic oxygen is not expected to occur, presumably CO_2 is lost as such. This means that 3 must rearrange to a species with two oxygens on the same carbon, and the formation of both dialdehyde 4 and indene (5) can be economically accommodated by the mechanism[6] indicated:



The rearrangement of 3 to 6 is analogous to that of bicyclo[2.2.1]-2,5-heptadiene epoxide to an analogue of 6,[7] and of certain aziridines corresponding to the bicycloheptadiene epoxide to aza analogues of 6.[8]

Acknowledgements

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References

1. For leading references, see E. Lewars and G. Morrison, Tetrahedron Letters, 501 (1977); E. Lewars and G. Morrison, Can. J. Chem., 55, 966 (1977), and references therein.
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4. M.J. Jorgenson, Tetrahedron Letters, 559 (1962).
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6. This mechanism is intended only to be suggestive; free-radical rather than ionic processes may be involved, and intermediates may interpose themselves in a process shown as being concerted.
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