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THERMOLYSIS OF BICYCLO[4.2.0]OCTA-3,7-DIENE-2,5-DIONES

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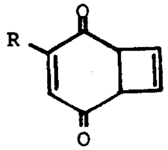
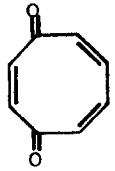
We have recently reported the synthesis of bicyclo[4.2.0]octa-3,7-diene-2,5-dione (1)[1] which is the valence bond isomer of the interesting but yet unknown cyclooctatriene-1,4-dione (cyclooctatetraeno-*p*-quinone) (2). As a good number of thermal transformation of cyclobutenes to 1,3-dienes have been known[2], it was expected that thermolysis of (1) would produce (2). We here report the results of thermolysis of (1) and its monobromo-derivative (4), 3-bromobicyclo[4.2.0]octa-3,7-diene-2,5-dione.



(1) R=H
(4) R=Br

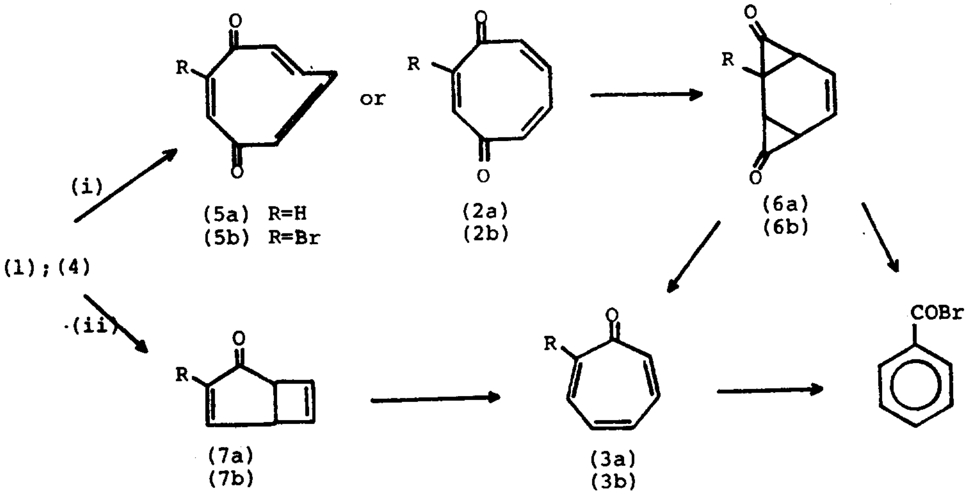


(2)

Compound (1) was quite stable up to 350°C on flash thermolysis[3] at 0.2 mm Hg. At 500°C, however, it gave, besides the unchanged material (8%), tropone (3a) (49%) and a trace amount of an unstable ketonic compound[4] which is not yet identified. The result is in agreement with that (1) shows a strong peak at m/e 106 (M-CO) in the mass spectrum[1].

Thermolysis of (4)[5] at the same condition adopted for (1) gave benzoyl bromide (22%) as the only isolable product.

As for the mechanism leading to tropone, two possible paths can be considered; (*i*) (1) at first undergoes ring opening to *trans*-cyclooctatriene-1,4-dione (5) or (2) which subsequently undergoes intramolecular Diels-Alder reaction to give the biscyclopropanone derivative (6) and then is decarbonylated; (*ii*) (1) is at first decarbonylated to bicyclo[3.2.0]hepta-3,6-diene-2-one (7) which subsequently, as already known[6], undergoes ring opening. Since, in our unpublished results, bicyclo[4.2.0]octa-7-ene-2,5-dione, the 3,4-dihydro derivative of (1), gives the expected ring-opened product, cycloocta-2,4-diene-1,6-dione, in good yield[7], the first path seems to be plausible. Benzoyl bromide may have been formed from (6b) or 2-bromotropone (3b); the latter compound has been reported to give it on thermolysis at 400-500°C[8].



Notes and References

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1) M. Oda, Y. Kayama, and Y. Kitahara, Tetrahedron Lett., 2019 (1974).

2) H. M. Frey "Advances in Physical Organic Chemistry" pp 147-193, 1966, Academic Press, London and New York, and references cited therein.

3) The thermolyses were carried out by passing the vapourized substrates through a pre-heated pyrex tube packed with quartz tips in vacuum.

4) This compound showed a carbonyl absorption at 1710 cm^{-1} and changed into an inseparable mixture (tlc) on standing.

5) This compound was prepared from (1) by bromination (1 equiv.) at -20°C in CCl_4 and subsequent treatment with NEt_3 in 89% yield; ν_{max} (neat)=1680, 1665, 1560 cm^{-1}; δ ($CDCl_3$)=7.18 (1H,d,J=0.9 Hz), 6.42(2H,s), 4.05(1H,d,3.4 Hz), 3.90 ppm (1H,dd,3.4 and 0.9 Hz).

6) P. R. Story and S. R. Fahrenholtz, J. Amer. Chem. Soc., 87, 1623 (1965). Reportedly, (4) undergoes ring opening to tropone at 350°C.

7) To be reported elswhere.

8) T. Mukai, T. Nakazawa, and K. Okayama, Tetrahedron Lett., 1695 (1968).