Thermal Rearrangement of Bicyclo[4.2.0]octa-4,7-diene-2,3-dione: Synthesis of Bicyclo[3.2.1]octa-3,6-diene-2,8-dione

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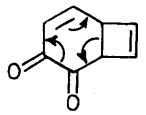
Summary Bicyclo[4.2.0]octa-4,7-diene-2,3-dione rearranges on heating at *ca.* 150 °C to bicyclo[3.2.1]octa-3,6-diene-2,8-dione which is in turn rapidly decarbonylated to tropone at 200 °C.

RECENTLY we described the synthesis of bicyclo[4.2.0]octa-4,7-diene-2,3-dione (**1**)[1] which is a valence isomer of the as yet unknown cyclo-octa-3,5,7-triene-1,2-dione (**2**). While examining the thermal behaviour of (**1**) as a potential precursor for (**2**), we found that (**1**) underwent a novel rearrangement.

When (**1**) was injected into a g.l.c. column (10% SE30, injection temperature 160 °C, column and detector temperatures 155 °C), a single peak was observed, due to bicyclo[3.2.1]octa-3,6-diene-2,8-dione (**3**) [pale yellow liquid; 11%; ν_{max} 1810m, 1772s, 1670s, and 1573m cm^{-1}; λ_{max} (ethanol) 224 (log ϵ 3·84), 275 (3·39), and 310sh (3·06) nm; δ (CCl$_4$) 3·63 (ddd, H-5, *J* 7·5, 3·3, and 1·0 Hz), 3·88 (ddd, H-1, *J* 3·8, 1·6 and 1·0 Hz), 5·93 (dd, H-3, *J* 9·5 and 1·6 Hz), 6.45 (dd, H-7, *J* 6·6 and 3·8 Hz), 6·83 (dd, H-6, *J* 6·6 and 3·3 Hz), and 7·38 (dd, H-4, *J* 9·5 and 7·5 Hz)].† The diketone (**3**) was also obtained in poorer yield by heating (**1**) in tetralin at 150 °C. Hydrogenation of (**3**) over Pd–C gave bicyclo[3.2.1]octane-2,8-dione.[2] The chemical shifts of the olefinic protons of (**3**) are *ca.* 0·1—0·6 p.p.m. lower than those reported for bicyclo[3.2.1]octa-3,6-diene-2-one.[3]

Since the arrangement of the π-orbitals of the 6-membered ring of (**1**) resembles that of cyclohexa-1,3-diene, the fairly easy rearrangement might be initiated by an electrocyclic ring-opening leading to the cleavage of the C–C bond of the α-diketone giving the *cis* unsaturated diketen (**4**). Intramolecular Diels–Alder reaction of (**4**) would lead to (**3**).

Injection of (**3**) into a g.l.c. column at 200 °C caused rapid decarbonylation and gave tropone (**5**) in high yield. Norbornadienones are known to undergo spontaneous cheletropic decarbonylation to give benzene.[4] In contrast, bicyclo[4.2.1]nona-2,4,7-trien-9-one was not decarbonylated even at 400 °C in spite of the presence of the cyclopent-3-en-1-one species suitable for thermal linear cheletropic decarbonylation.[5] Although only qualititative at this stage, the ease with which the decarbonylation of (**3**) takes place is comparable to that for norbornen-7-ones[6] in spite of the possibility that the release of strain energy in (**3**) by decarbonylation is less than that in norbornen-7-ones. This may reflect some aromatic stabilisation of tropone which is formed.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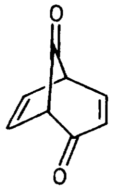
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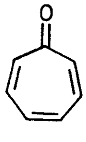
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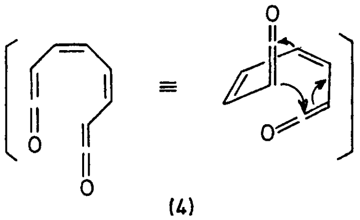
(4)

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† Most of (**1**) polymerised by decomposition, leaving a black solid in the injection part.

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[2] H. Kato, N. Miyamoto, M. Kawanishi, and N. Nozaki, *Tetrahedron*, 1970, **26**, 2975.
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[5] K. Kurabayashi and T. Mukai, *Tetrahedron Letters*, 1972, 1049.
[6] C. F. H. Allen, *Chem. Rev.*, 1962, **62**, 653; M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *ibid.*, 1965, **65**, 261; S. C. Clarke and B. L. Johnson, *Tetrahedron*, 1971, **27**, 3555.