

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

By (the late) YOSHIO KITAHARA, MASAJI ODA,* and MITSUNORI ODA

(Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan)

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 in turn rapidly decarbonylates to tropone at 200 °C.

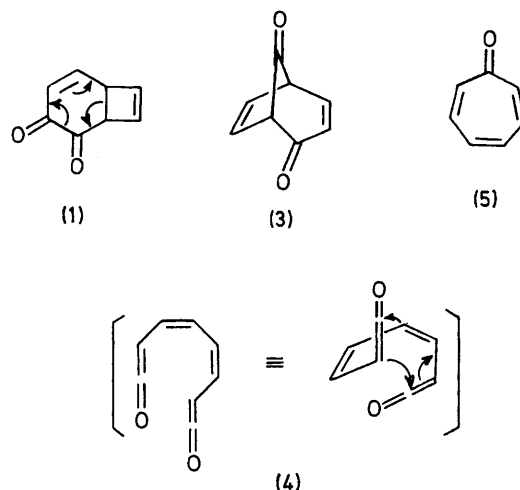
RECENTLY we described the synthesis of bicyclo[4.2.0]octa-4,7-diene-2,3-dione (**1**)¹ which is a valence isomer of the as yet unknown cyclo-octa-3,5,7-triene-1,2-dione (**2**). While examining the thermal behaviour of (**1**) as a potential precursor for (**2**), we found that (**1**) underwent a novel 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 diketene (**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 qualitative at this stage, the ease with which the decarbonylation of (**3**) takes place is comparable to that for norbornen-7-ones⁶ 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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† Most of (**1**) polymerised by decomposition, leaving a black solid in the injection part.

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³ P. K. Freeman and D. G. Kuper, *Chem. and Ind.*, 1965, 424.

⁴ S. Yankelevich and B. Fuchs, *Tetrahedron Letters*, 1967, 4945, and references therein.

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.