Tetrahedron Letters, Vol.31, No.50, pp 7341-7342, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

NOVEL THERMAL DECARBONYLATIVE DIMERIZATION OF 1,2,3,4,5,6-HEXAHYDROBENZO[1,2;4,5]DICYCLOBUTENE-3,6-DIONE

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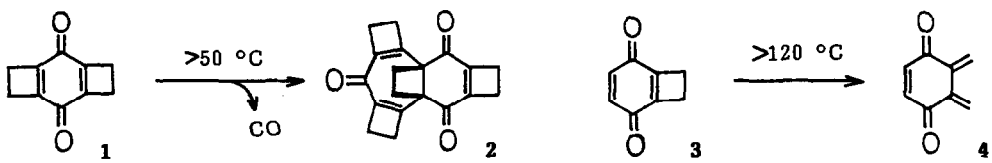
Abstract: The title compound **1**, a strained p-benzoquinone due to cyclobutene annelation, affords novel decarbonylated dimer **2**, with unusual easiness, upon heating either at solid or in solution.

p-Benzoquinones are thermally fairly stable and undergo decarbonylative fragmentations only at high temperatures (>800 °C).[1] In the course of our studies on p-benzoquinones fused with small rings, we have encountered unusually ready thermal decarbonylative dimerization of the title compound **1** (dicyclobuta-p-benzoquinone), a strained p-benzoquinone derivative.[2]

When the yellow fine needles of quinone **1** were heated above 50 °C at solid state, the crystals gradually turned pale yellow with concomitant evolution of a gas, carbon monoxide. The transformation completed within 1.5 h at 80 °C and gave decarbonylated dimer **2** in 88% yield. The same dimer was also obtained upon heating in solutions, although the reaction was slower (87% conversion after 12 h at 80 °C at 0.5 M in benzene; 53% yield).

The structure of **2** was deduced from its spectral data[3] and confirmed by X-ray crystallographic analysis (Fig. 1).[4] Dimer **2** retains all the four-membered rings present in **1**, and therefore the transformation goes through without involving ring-opening of the cyclobutenes. This is in sharp contrast with the thermal behavior of monocyclobuta-p-benzoquinone **3** which yields dimers above 120 °C via ring-opened intermediate **4**.[5]

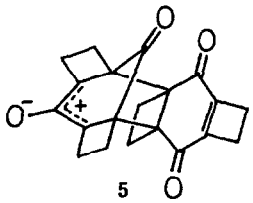


1 **2** **3** **4**

Differential thermal analysis (DTA) of **1** (Fig. 2) shows a broad exothermic peak between ca. 70-120 °C and then a fairly sharp endothermic peak at 147 °C, the latter corresponding to the melting point of **2**, after which an exothermic reaction again follows probably due to ring-opening of the cyclobutene ring(s) of **2**. Thermogravimetric analysis of **1** indicated concomitant loss of carbon monoxide with the first exothermic process (6.7%

total loss in weight vs. 8.7% theory). On the other hand, DTA of quinone **3** showed a normal sharp peak of melting point at 75°C and thereafter an exothermic process but only above 120 °C (ring-opening of the cyclobutene).

A possible pathway for **2** starts from dimerization of **1** by homo-Diels-Alder reaction giving **5** as the key intermediate from which decarbonylation would be easy. Such a dimerization is not precedented at all in the thermal reactions of p-benzoquinones. Although strain in **1** should play an important role in the present unusual transformation, further studies are to be continued for deeper understanding.



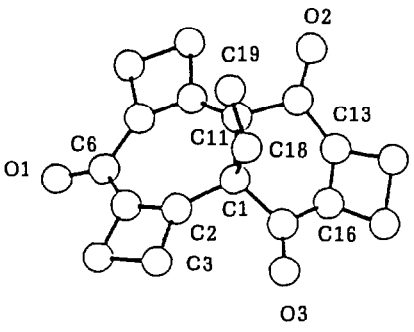


Fig. 1 The molecular drawing of **2** from X-ray crystallographic analysis.

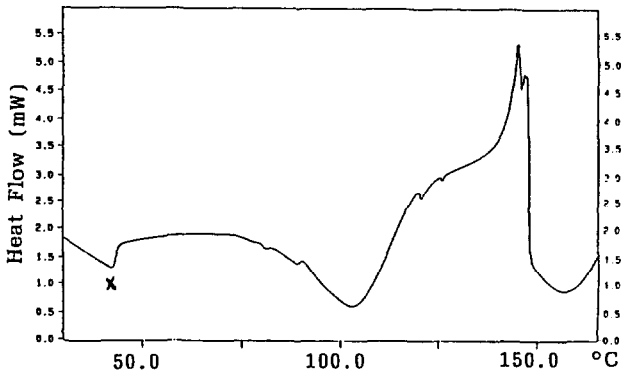


Fig. 2 The differential scan calorimetry of **1** (temperature increase: 3.0°C/min).

Acknowledgement: We are grateful to Prof. Hiroshi Suga and Dr. Osamu Yamamuro (Osaka Univ.) for their help in DTA and thermogravimetric analysis. This work was partially supported by the Grant-in-Aid for Scientific Research on Priority Areas No. 01648003 from the Ministry of Education, Science and Culture, Japan.

References and Notes

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2) Y. Kanao, M. Iyoda, and M. Oda, Tetrahedron Lett., **24**, 1727 (1983); M. Iyoda, T. Yamauchi, and M. Oda, J. Chem. Soc., Chem. Commun., **1986**, 303.
3) IR (KBr): ν 1695, 1665, 1630 cm^{-1}; UV (EtOH): λ_{max} 254 (log 4.30), 319 nm (3.20); ^1H NMR ($CDCl_3$): δ 2.52 (m, 8H), 2.70 (m, 4H), 3.00 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 24.26 (t), 27.70 (t), 28.93 (t), 34.67 (t), 61.32 (s), 140.86 (s), 153.97 (s), 157.86 (s), 180.97 (s), 190.60 (s).
4) Crystallographic data will be deposited at the Cambridge Crystallographic Data Centre. Structure factors may be obtained from one of us (L-K. L.).
Crystal data of **2**: $C_{19}H_{16}O_3$, Mr = 292.33, orthorhombic, space group P ccn, a= 15.665(2), b = 19.350(2), c = 9.460 (0) Å, U = 2867.5 (7) Å, Z = 8, Dc = 1.354 g/cm^{-3}, F(000) = 1231.86. Nonius CAD-4 data, Mo-Kα radiation, λ 0.7093 Å, mu = 0.08 mm^{-1}, min. and max. transmission factors 0.969 and 1.000. Final residuals R = 0.039, Rw = 0.041, GoF = 1.61 from 38 atoms, 263 parameters and 1536 out of 2521 measured reflections, (2σ cut-off for observations).
Some bond lengths are: O(1)-C(6) 1.229, O(2)-C(12) 1.210, C(2)-C(5) 1.342, C(3)-C(4) 1.559, C(13)-C(16) 1.337, C(1)-C(11) 1.585, C(18)-C(19) 1.524 Å.
5) Y. Kanao and M. Oda, Bull. Chem. Soc. Jpn., **57**, 615 (1984).

(Received in Japan 25 August 1990)