X-Ray-induced Retro [2+2] Cycloaddition of a *syn*-Tricyclo[4.2.0.0^{2,5}]octane Derivative to a *cis,cis*-Cycloocta-1,5-diene Derivative within a Single Crystal Lattice

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A *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative **1**, obtained from the high-pressure cycloaddition reaction of dimethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **3** with cyclooctatetraene **4**, isomerizes on exposure to X-ray radiation to a *cis,cis*-cycloocta-1,5-diene derivative **2** without disrupting the crystal structure.

It is known that the *p*-bromophenacyl ester of hirsutic acid undergoes an unusual solid-state reaction, isomerization of an epoxy group to an allyl alcohol on exposure to X-ray radiations,[1] whilst retaining the original crystallographic parameters. Solid-state chemical reactions, *i.e.* 'single crystal-to-single crystal transformations'[2] have been paid much attention in various respects. Herein reported is the isomerization of a *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative **1**† to a *cis,cis*-cycloocta-1,5-diene derivative **2**† in a retained single crystal.

A toluene solution of dimethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **3** and cyclooctatetraene **4** was heated at 100 °C under 1000 MPa to give two 2:2 adducts ($C_{40}H_{44}O_{10}$, *m/z* 684) (**1**, 37%, **2**, 2%) together with (**5**, <1%; **6**, 1%; **7**, 30%; **8**, 5%).‡ The ^{1}H NMR spectra of **1** and **2** indicated highly symmetrical structures.

When a single crystal of **1**,§ obtained by recrystallization from a mixture of cyclohexane and chloroform, was exposed to X-rays, the intensity of one of the monitoring reflections for data collection gradually decreased. After 6 h, the intensity of the reflection became nearly constant to make it possible to collect three-dimensional intensity data. The monoclinic lattice parameters before data collection are in good agreement with those after data collection within 1% difference.¶ It was suggested that a structural change occurred in a cell unit without degradation of crystallinity. The crystal structure is shown in Fig. 1. The bond lengths of C(8)–C(9) and C(20)–C(21) are 1.31(1) Å and the distances between C(8) and C(21) and C(9) and C(20) are 2.69(1) Å, which indicated that the crystal has a cycloocta-1,5-diene structure.‖

The ^{1}H NMR spectrum of the sample collected after X-ray radiation was the same as that of **2**; no signals ascribable to **1** were observed anymore. Taking the ^{1}H NMR spectral changes into account and considering only the minor changes in lattice parameters during the X-ray radiation, the structure of **1** was identified to be the *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative. Therefore, it is clear that a single crystal of **1** was transformed into a single crystal of **2** during X-ray radiation.

Compound **2** was formed in 40% yield when **1** was heated in a chlorobenzene solution at 120 °C for 43 h. No reaction occurred when **1** was heated at 130 °C for 40 min in the solid state. However, by heating **1** at 140 °C for 1 h in the solid state, the ^{1}H NMR spectrum of the thermolysate indicated that the ratio of **1** and **2** was 1:1.2.[3] When **1** was irradiated, both in methanol with a low-pressure mercury lamp through a quartz filter and in acetone with a high-pressure mercury lamp through a Pyrex filter, only polymeric materials were formed.

Crystalline **1** was analysed by thermogravimetry/differential thermal analysis (TG/DTA). As shown in Fig. 2, a mass loss of 15.6% occurs in a single step between 99 and 114 °C, which is in good agreement with the removal of 1.5 mol of cyclohexane.

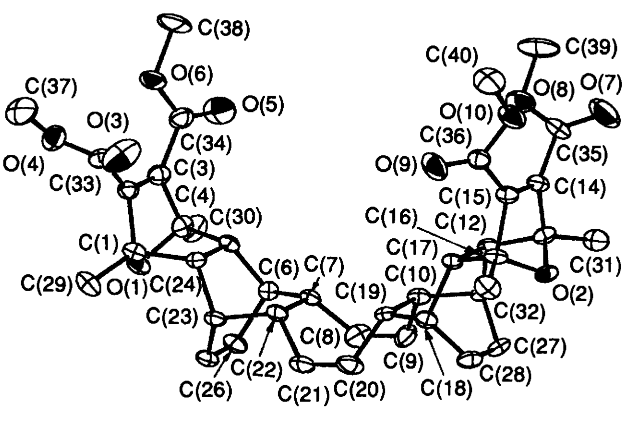
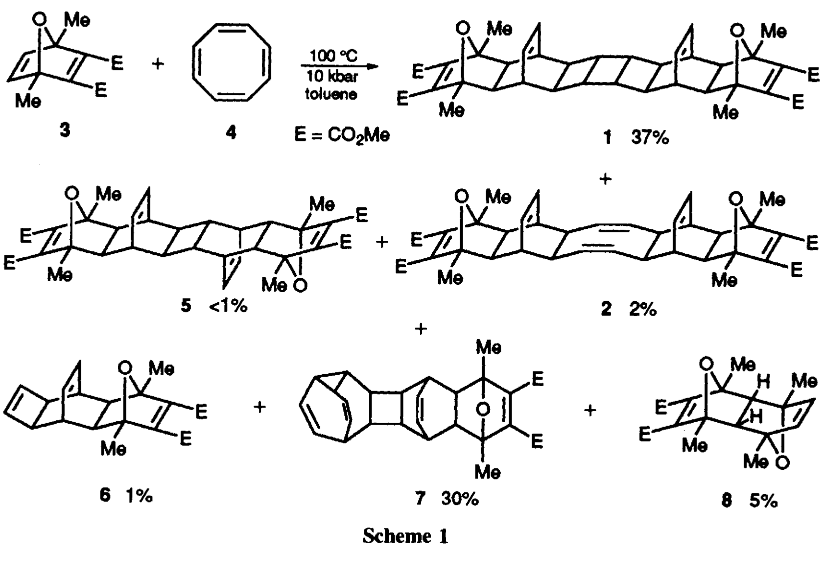


Fig. 1 ORTEP drawing of the cyclooctadiene derivative, derived from the tricyclooctane derivative by X-ray exposure, with thermal ellipsoids scaled to enclose 30% probability. Oxygen atoms are shown as cross-hatched and hydrogen atoms are not shown.



Scheme 1

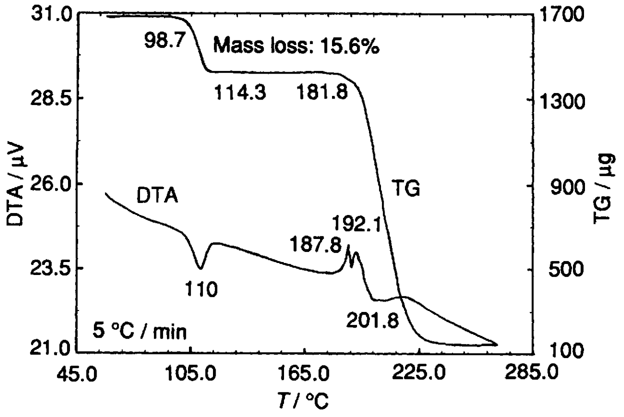


Fig. 2 DTA and TGA thermograms for 3 : 2 cyclohexane complex of **1**

At *ca.* 182 °C, a large mass loss is observed due to retro-Diels–Alder reaction.[**]

In conclusion, the X-ray-induced retro [2 + 2] cycloaddition of a tricyclooctane ring to a cyclooctadiene system has taken place in a crystal lattice. It may be interpreted that the deformation of the crystal lattice caused by the structural change of crystalline **1** into crystalline **2** could be negligible since the reaction occurred in the centre of the molecule and the bulky substituents would keep the intermolecular distance approximately constant during the reaction. Thus, relaxation of the local stress generated in the crystal should occur with minimal atomic and molecular rearrangement.

Received, 22nd November 1993; Com. 3/06960E

Footnotes

[†] Full name: of **1**, tetramethyl 1,4,4*a*,5,5*a*,5*b*,5*c*,5*d*,6,6*a*,7,10,10*a*,11,11*a*,11*b*,11*c*,11*d*,12,12*a*-eicosahydro-1,4,7,10-tetramethyl-1,4 : 7,10-diepoxy-5,12 : 6,11-diethenocyclobuta[1″,2″ : 3,4;3″,4″ : 3′,4′]-dicyclobuta[1,2-*b* : 1′,2′-*b*′]dinaphthalene-2,3,8,9-tetracarboxylate; of **2**: tetramethyl 1,4,4*a*,5,5*a*,7*a*,8,8*a*,9,12,12*a*,13,13*a*,15*a*,16,16*a*-hexadecahydro-1,4,9,12-tetramethyl-1,4,4 : 9,12-diepoxy-5,16 : 8,13-diethenocycloocta[1,2-*b* : 5,6-*b*′]dinaphthalene-2,3,10,11-tetra-carboxylate.

[‡] The synthetic aspect of the reaction and the structure determination will be described in a full paper.

[§] Single crystal X-ray diffraction data were collected on an Enraf-Nonius diffractometer (Cu-Kα radiation) using ω-2θ scan technique. Cell parameters before data collection: a = 15.953(4), b = 10.543(1), c = 26.181(3) Å, β = 95.66(1)°, V = 4382.2 Å^3, space group $P2_1/n$. Of the 8226 reflections measured, 7461 were unique and not systematically absent. Using the 3952 reflections having intensities greater than 3.0 times of their standard deviations, 629 variable parameters were refined to give R = 0.110 and Rw = 0.127. The somewhat large R factors can be attributed to the disordered contributions of the included solvent molecules and the methyl hydrogens of methoxycarbonyl groups, which could not be analysed precisely because of their large mobilities in the channel structure. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[¶] Cell parameters after data collection: a = 15.950(5), b = 10.543(2), c = 26.370(6) Å, β = 95.72(2)°.

[||] The X-ray analysis disclosed that two molecules make a cavity to include three molecules of cyclohexane used for recrystallization solvent.

[**] When **1** was heated in the solid state at 160 °C for 10 h in a sealed tube, the ^{1}H NMR spectrum of the thermolysate revealed formation of benzene, **3**, and dimethyl 1,4-dimethylfuran-3,4-dicarboxylate in a ratio of 0.85 : 0.3 : 1 *via* retro-Diels-Alder reactions.

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3 Similar [2 + 2] cycloreversions have been observed in the thermal reaction of *syn*-tricyclo[4.2.0.0^{2,5}]octane derivatives; G. Schröder and W. Martin, *Angew. Chem.*, 1966, **78**, 117; G. I. Fray and R. G. Saxon, *Tetrahedron Lett.*, 1973, 3579.