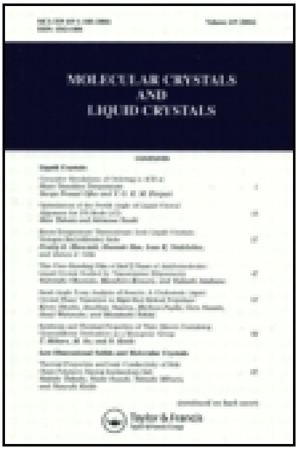

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Single Crystal-To-Single Crystal Transformation of A Syn -Tricyclo[4.2.0.0 2,5]Octane to A (Z , Z)-Cycloocta-1,5-Diene Under X-Ray Irradiation

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SINGLE CRYSTAL-TO-SINGLE CRYSTAL TRANSFORMATION OF A *SYN*-TRICYCLO[4.2.0.0^{2,5}]OCTANE TO A (*Z*,*Z*)-CYCLOOCTA-1,5-DIENE UNDER X-RAY IRRADIATION

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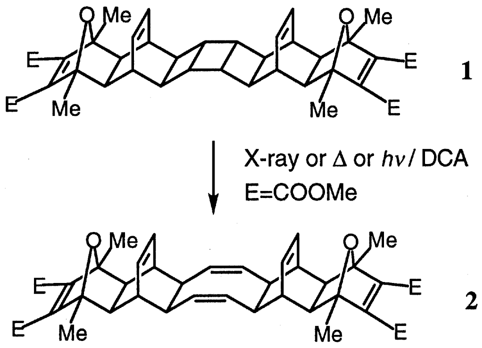
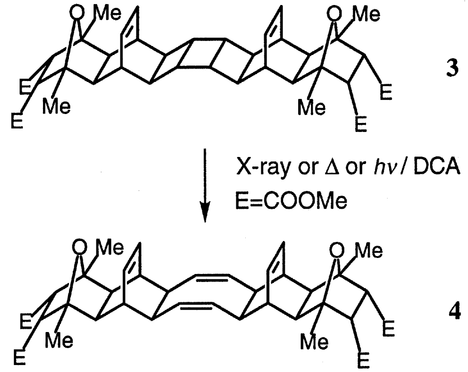
*We have observed that a syn-tricyclo[4.2.0.0^{2,5}]octane derivative (***1***) isomerized keeping the single crystalline state to a (Z,Z)-cycloocta-1,5-diene derivative (***2***) during the X-ray crystallographic analysis. In this paper, we report that an octahydro derivative (***5***) of* **1** *transformed to a (Z,Z)-cycloocta-1,5-diene derivative (***6***) keeping the single crystalline state. Similarly, irradiation of an acetonitrile solution of* **5** *with high-pressure mercury lamp (>400 nm) in the presence of a sensitizer, 9,10-dicyanoanthracene, gave* **6** *in good yields via a radical cation mechanism.*

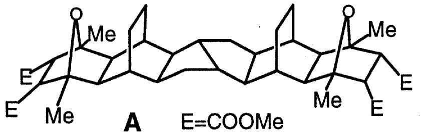
Keywords: single crystal-to-single crystal reactions; *syn*-Tricyclo[4.2.0.0^{2,5}]octanes; radical cation mechanism; electron-transfer reactions; 9,10-dicyanoanthracene

INTRODUCTION

Recently, much attentions have been paid on solid state reactions because they are solvent-free, clean, and economical reactions [1]. Among them, single crystal-to-single crystal (SC-to-SC) reactions, although they are limited, are quite attractive because the whole reaction pathway can be visualized through X-ray crystallographic analysis. Most examples involve the photochemical dimerizations [2] and thermal reactions [3]. Previously, some examples of SC-to-SC transformations induced by X-ray irradiation have been observed in racemization of the chiral cyanoethyl group in a cobaloxime complex crystal [4] and in the determination of the structure of the *p*-bromophenacyl ester of hirsutic acid [5,6].







We have reported a SC-to-SC transformation of a *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative (**1**) to a (*Z*,*Z*)-cycloocta-1,5-diene derivative (**2**) under the X-ray crystallographic analysis [7]. The same transformation from **1** to **2** was observed in thermal reactions in solid state as well as in chlorobenzene at 130°C along with the retro Diels-Alder reaction products. In the case of a tetrahydro derivative (**3**) of **1**, **3** isomerized to a (*Z*,*Z*)-cycloocta-1,5-diene derivative (**4**) in thermolysis in solid state and by means of X-ray irradiation without keeping a single crystalline state [8]. We have also reported that a catalytic hydrogenation(H_2/Pd-C) product of **1**, which was assigned to be an octahydro derivative, was quite stable toward X-ray irradiation and thermolysis [8]. But the structure was mistaken and should be revised to a bicyclo[3.3.0]octane derivative (**A**), a decahydro isomer, from the spectral data [9].

In this paper, we prepared octahydro derivative (**5**) [10] of **1** to investigate transformation to a (*Z*,*Z*)-cycloocta-1,5-diene derivative (**6**) [11] induced by the X-ray irradiation as well as thermal and photo-induced reactions in the presence of 9,10-dicyanoanthracene (DCA).

RESULTS AND DISCUSSION

A single crystal of octahydro derivative **5**, prepared from **1** by catalytic hydrogenation (H_2/PtO_2) in 86% yield, was obtained in a mixed solvent of chloroform and cyclohexane. X-ray crystallographic analysis of a single crystal of **5** at room temperature indicated that the transformation from **5** to **6** occurred keeping the single crystalline state. In a unit cell, four molecules of **6** included three molecules of cyclohexane as inclusion solvents. In Figure 1, the lattice parameter changes of **5** to **6** during irradiation are shown, in which the changes of the values V and γ are large.

On the other hand, X-ray analysis of a single crystal of **5** at −150°C showed a *syn*-tricyclooctane structure as shown in Figure 2. The ring opening of the central cyclobutane ring was depressed by lowering temperature. The relatively high R value is due to disordering of cyclohexane molecules included [12].

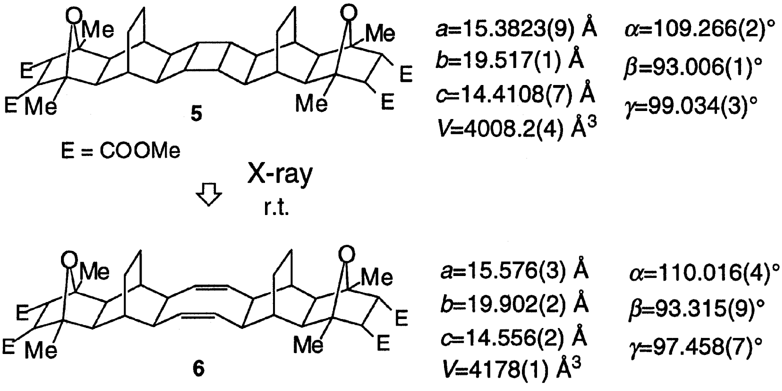
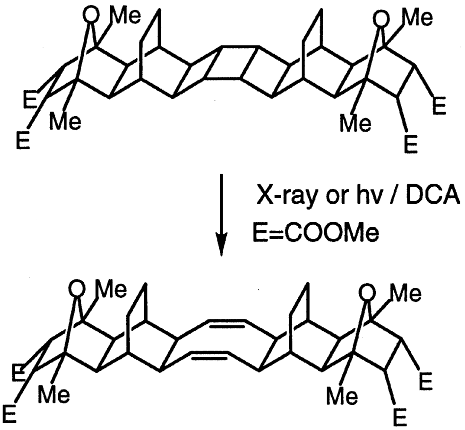


FIGURE 1 Lattice parameter changes during transformations.



5

6

It is known that tetraphenyltricyclo[4.2.0.0^{2,5}]octane (**7**) gave a cycloocta-1,5-diene derivative (**8**) by means of thermal reactions [13] as well as irradiation in the presence of DCA [14].

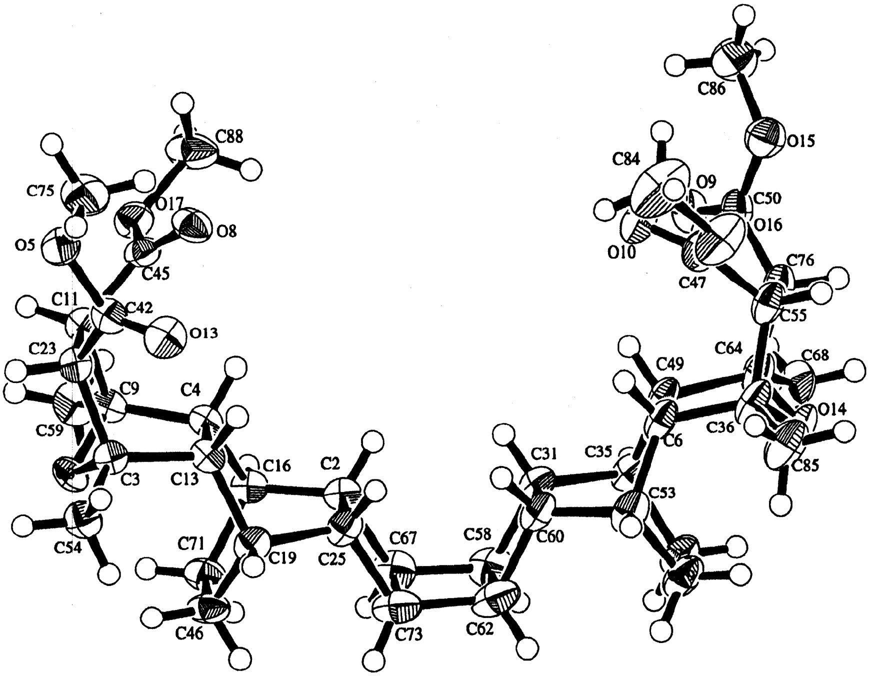
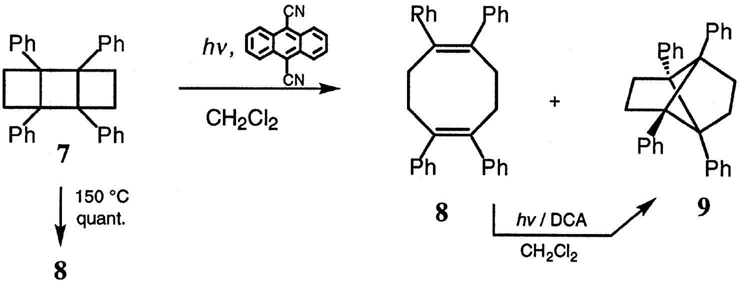


FIGURE 2 ORTEP drawing of octahydro derivative **5** at −150°C.

When compound **5** was heated at 130°C in DMSO, compound **6** was obtained in quantitative yield. Next, a $CDCl_3$ solution of **5** was irradiated in the presence of DCA by a 400 W high pressure mercury lamp through a filter to cut off light of $\lambda < 400$ nm to give cycloocta-1,5-diene **6** in 84% yield. The reaction was monitored by NMR spectra.



The photochemical reaction proceeded exothermically since ΔG value for electron transfer from **5** to DCA was calculated to be −5.5 kcal/mol by the Weller equation [15] using the oxidation potential of **5** ($E^{ox}{}_{1/2} = 1.74\ V$) [16] and the reduction potential of DCA ($E^{re}{}_{1/2} = 0.89\ V$) [17]. Similarly, compounds **1** and **3** gave **2** in 93% and **4** in 96%, respectively by the photolysis in the presence of DCA.

syn-Tricyclo[4.2.0.0^{2,5}]octanes, thus, transformed to (*Z*,*Z*)-cyclo octa-1,5-dienes by means of thermolysis, photolysis in the presence of DCA, and X-ray irradiation. The transformations of tricyclooctanes to cyclooctadienes are not thermally-allowed, concerted reactions according to the Woodward-Hoffmann rule [18]. The thermal reactions, therefore, would proceed via a diradical intermediate. In the case of photolysis, electron-transfer process would be an initial step to give a radical cation, which gives cyclooctadienes.

The mechanism of the transformation by means of X-ray irradiation should be worth discussing. There are two possibilities; one is a diradical mechanism and the other is a radical cation mechanism. In order to proceed via a diradical species, it would be required to induce the temperature above 100°C, which induced thermolysis to give cycloocta-1,5-dienes, by X-ray irradiation even though it is a local temperature. It might not be the case. Therefore, a radical cation mechanism would be plausible. The analyzing X-ray beam liberated an electron to form a radical cation. However, we observed that the temperature also played a role in the ring-opening of the central cyclobutane ring of *syn*-tricyclooctanes, that is, analysis of tricyclooctanes at room temperature gave rise to cycloocta-1,5-diene structures whereas analysis at −150°C did not induce ring-opening. It is explained that the reactivity of the radical cation should be dependent on temperature. At lower temperature, the radical cation formed from tricyclooctanes has not enough activation energy for the ring opening reaction to lead cycloocta-1,5-dienes in solid state.

From these evidences, a chain reaction propagated by the radical cation is more plausible in the X-ray induced SC-to-SC transformation of compound **5**, which has not any heavy atom although it was excluded as the mechanism in the rearrangement of *p*-bromophenacyl ester of hirsutic acid [6]. The transformations from *syn*-tricyclo[4.2.0.0^{2,5}]octanes to cyclo octa-1,5-dienes occurred at the center of the molecules and the molecules have relatively bulky substituents at the terminal positions to keep the distance from the neighboring molecules, which helped not to disrupt the crystal packing during ring-opening of the central cyclobutane ring under X-ray irradiation. Furthermore, the single crystal included solvents, which would act as a shock-absorber to relieve strains. Thus, the present systems have some structural advantages, which made it possible to undertake the SC-to-SC reactions.

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[9] Data of **A**: colorless crystals, mp >300°C; ^{1}H NMR ($CDCl_3$) δ : 1.10 (2H, dm, $J = 12$ Hz), 1.55 (4H, m), 1.57 (12H, s), 1.6–1.9 (10H, m), 2.1 (2H, m), 2.14 (2H, s), 2.21 (2H, br s), 2.37 (2H, s), 2.66 (2H, br s), 3.03 (4H, s), 3.70_5 (6H, s) and 3.71_3 (6H, s); ^{13}C NMR ($CDCl_3$) δ: 15.7 (2C), 16.3 (2C), 18.26 (2C), 18.34 (2C), 26.4 (2C), 27.0 (2C), 30.2 (2C), 30.9 (2C), 32.1 (2C), 36.8 (2C), 43.8 (2C), 45.9 (2C), 51.71 (2C), 51.74 (2C), 56.80 (2C), 56.84 (2C), 86.76 (2C), 86.82 (2C), 171.4 (2C), and 171.5 (2C); IR (KBr) ν: 2950, 1744, 1633, 1435, 1435, 1381, 1209, 1081, and 863 cm^{-1}; MS (FAB) m/z (%): Found: 695 (M^+ + 1, 18), 663 (5), 645 (11), 91 (16); Calcd for $C_{40}H_{55}O_{10}$: 695.

[10] Data of **5**: colorless crystals, mp 288°C; ^{1}H NMR ($CDCl_3$) δ : 1.55 (4H, s), 1.57 (12H, s), 1.69 (8H, m), 2.29 (4H, s), 2.82 (4H, s), 3.05 (4H, s), 3.07 (4H, s), and 3.72 (12H, s); ^{13}C NMR ($CDCl_3$) δ : 16.5 (4C), 18.4 (4C), 27.4 (4C), 37.3 (4C), 38.7 (4C), 43.3 (4C), 51.8 (4C), 56.8 (4C), 86.9 (4C), and 171.4 (4C); IR (KBr) ν: 2952, 1743, 1435, 1351, 1206, 1149, 1079, 1030, 888, 863, and 752 cm^{-1}; MS (FAB) m/z (%): 693 (M^{+} + 1, 70), 661 (56), 643 (45), 243 (48), 113 (65), and 91 (51); HRMS (FAB): Found: 693.3638; Calcd for $C_{40}H_{53}O_{10}$: 693.3639.

[11] Data of **6**: colorless crystals, mp 288°C; ^{1}H NMR ($CDCl_3$) δ : 1.55 (8H, m), 1.56 (12H, s), 1.73 (4H, m), 2.39 (4H, s), 2.67 (4H, br s), 3.05 (4H, s), 3.71 (12H, s), and 5.70 (4H, s); ^{13}C NMR ($CDCl_3$) δ: 15.2 (4C), 18.1 (4C), 29.5 (4C), 41.2 (4C), 44.7 (4C), 51.7 (4C), 56.8 (4C), 86.8 (4C), 132.6 (4C), and 171.1 (4C); IR (KBr) ν: 2950, 2892, 1744, 1472, 1435, 1640, 1381, 1350, 1209, 1149, 1081, 1028, 897, 864, and 768 cm^{-1}; MS (FAB) m/z (%): 693 (M^{+} + 1, 47), 661 (37), 165 (36), and 91 (47); HRMS (FAB): Found: 693.3637; Calcd for $C_{40}H_{53}O_{10}$: 689.3639.

[12] Lattice parameters of a single crystal of $\mathbf{5}_2$ •cyclohexane$_{1.5}$ at −150°C: $(C_{40}H_{52}O_{10})_2 \bullet (C_6H_{12})_{1.5}$, triclinic, P1, a = 15.3859(9) Å, b = 19.517(1) Å, c = 14.4108(7) Å, α = 109.266(2)°, β = 93.006(1)°, γ = 99.034(3)°, V = 4008.2(4) Å^3, Z = 2, M_r = 1511.93, D_x = 1.253 g/cm^3, R = 0.154, ωR = 0.312.

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[16] Oxidation potential (E^{ox} / V *vs* SCE) of **1** was observed in acetonitrile with 0.1 mol dm^{-3} Et_4NClO_4 by means of cyclic voltammetry at room temperature. A Pt disk and a Pt wire electrode were used as a working and counter electrode, respectively.

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