High-Pressure Diels–Alder Reaction of Cyclooctatetraene with Dimethyl 1,4-Dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate. Single Crystalline State Valence Isomerization of a *syn*-Tricyclo[4.2.0.0^{2,5}]octane Derivative

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(Received March 15, 1995)

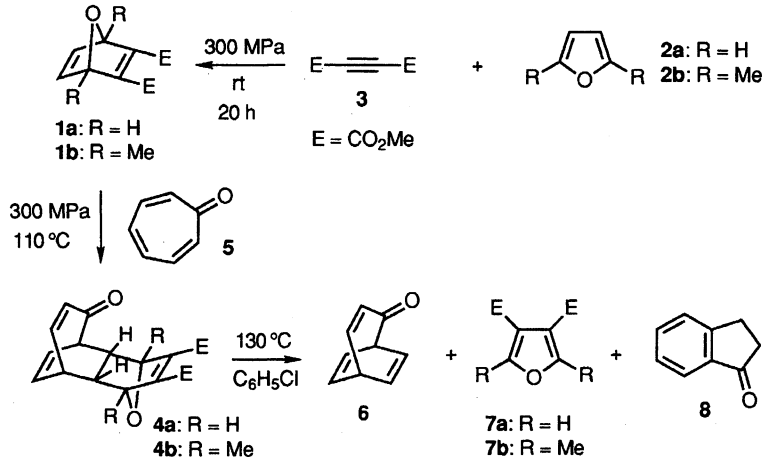
High-pressure Diels–Alder reaction of cyclooctatetraene with dimethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate afforded six products, one of which was shown to be a 2 : 2-adduct having a *syn*-tricyclo[4.2.0.0^{2,5}]octane framework. Upon radiation with X-rays, the tricyclooctane derivative isomerized to a cyclooctadiene derivative.

Previously, we have shown that dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**1a**), the Diels–Alder adduct of furan (**2a**) to dimethyl butynedicarboxylate (**3**), behaves as a good acetylene synthone.[1,2] Even better is its dimethyl derivative, dimethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**1b**); the Diels–Alder adduct (**4b**) of tropone (**5**) to **1b** was quantitatively cycloreversed to homobarrelenone (**6**) as well as dimethyl 2,5-dimethylfuran-3,4-dicarboxylate (**7b**)[2] without being contaminated by 1-indanone (**8**), whereas the thermolysis of the Diels–Alder adduct (**4a**) from **1a** and **5** was shown to give a considerable amount of **8** (Scheme 1).[1]

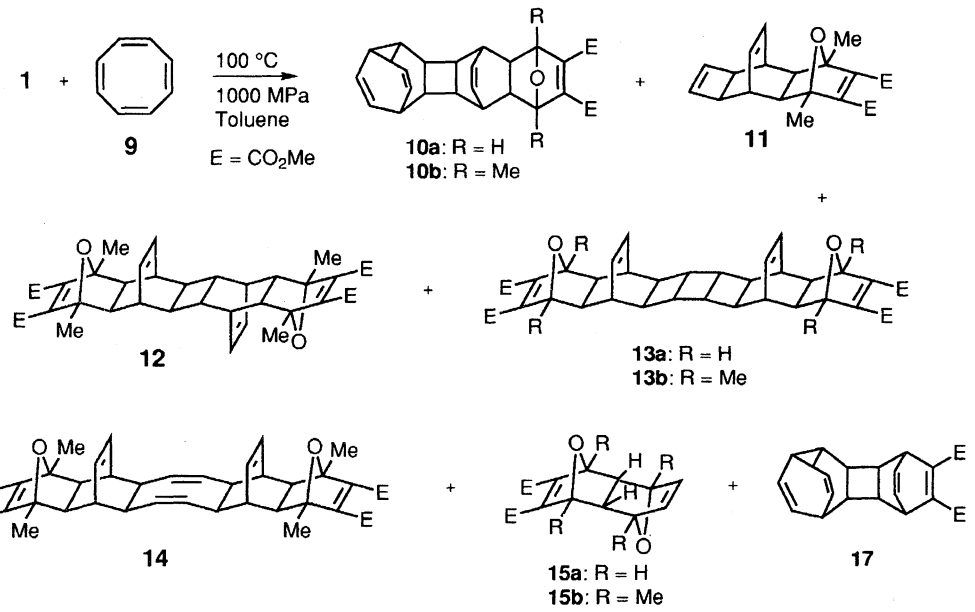
Extending the reaction of **1b** with cyclooctatetraene (**9**), we now find some novel features of valence isomerization[3] as described herein.

Results and Discussion

High-Pressure Cycloaddition Reactions of 1b, 1a, and 3 with 9. When a toluene solution of **1b** and **9** was heated at 100 °C under 1000 MPa, six products (**10b**, **11**, **12**, **13b**, **14**, and **15b**) were obtained (Scheme 2); the structure of **15b** was a 2 : 1-cycloadduct of 2,5-dimethylfuran to **3**.[2] The least polar product (**10b**) was a 2 : 1-adduct of **9** to **1b** and its ^{1}H NMR spectrum revealed characteristic signals of homotropylidene-type triplets at δ=5.68 (1H, t, J=9.3 Hz) and 5.88 (1H, t, J=9.3 Hz). The symmetrical nature of the molecule together with other chemical shift data allowed its structure to be deduced as depicted.



Scheme 1.



Scheme 2.

The product **11** was a 1 : 1-cycloadduct having a cyclobutene moiety; its ^{1}H NMR spectrum revealed a good parallelism with the Diels–Alder adduct (**16**) of **9** to maleic anhydride, a precursor of basketane,[4] and the chemical shift of its methine protons ascribable to those on the carbons adjacent to the ethereal carbons, δ=2.03, suggested the structure shown. The molecular composition of **12** suggested a loss of a four carbon unit from a 2 : 2-adduct. Thus, under those high-pressure conditions, the *retro*-Diels–Alder process occurred to give further fragmentation products.

However, due to the highly symmetrical nature, the structure assignments of **12**, **13b**, and **14** from the NMR spectral analysis were difficult. Therefore, the X-ray crystallographic analyses were performed as will be described in a later section.

Since some of the products are indicated to be secondary products, the pressure effect of the cycloaddition step was analyzed in a different pressure range; thus, under the higher pressure, yields of **11**, **12**, and **15b** were decreased, while that of **10b** increased (Table 1).

In order to evaluate the effect of two methyl groups, the high-pressure Diels–Alder reaction of **9** with **1a** was also carried out; four products (**10a**, **17**,[5] **13a**, and **15a**) were obtained. The ^{1}H NMR spectra of **10a** and **13a** were similar to those of **10b** and **13b** except for lacking the signals of the methyl groups on the 7-oxanorbornene moiety. Thus, their structures could be assigned as depicted. It is interesting that from **9** and **1a**, no 1 : 1-product such as **11** was detectable; therefore, under the compressed conditions, **9** should dimerize prior to cycloaddition.

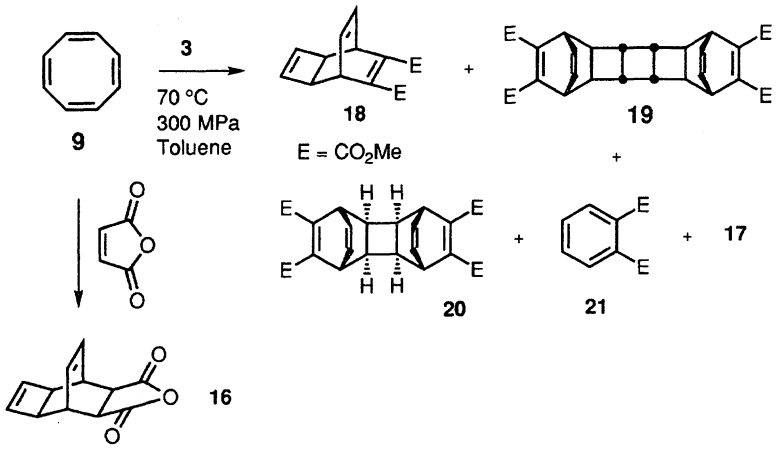
Table 1. Pressure Dependence of Product Distributions for the Reaction of **1b** and **9**

Pressure/MPa	Conversion/%	Yields/%					
		10b	**11**	**12**	**13b**	**14**	**15b**
1000	78	30	1	<1	37	2	5
300	75	25	10	6	37	2	9

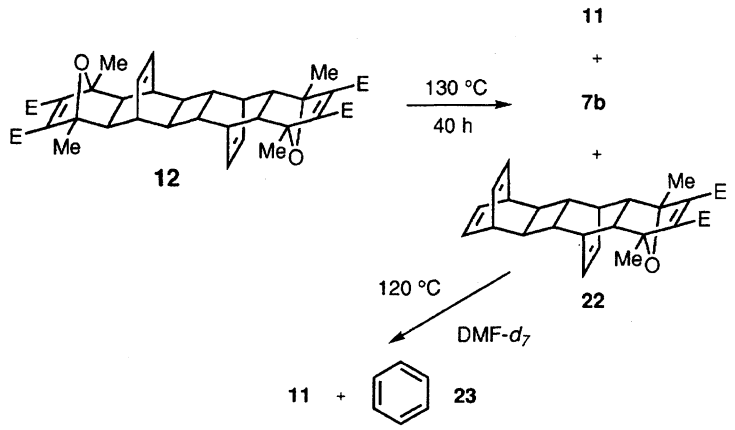
Moreover, the high-pressure Diels–Alder reaction of **3** and **9** also revealed a predominance of cycloadducts derived from dimers of **9**,[6,7] i.e., dimethyl tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene-7,8-dicarboxylate (**18**)[7] was only the product derived from monomeric **9**; others (**17**, **19**, and **20**) were derived from dimers of **9** (Scheme 3). The formation of dimethyl phthalate (**21**) indicates that a *retro*-Diels–Alder process occurred. At the same time, the formation of **17** and **15a** in the reaction of **1a** and **9** indicated a partial fragmentation of **1a** to **3** and **2a** under 300 MPa.

Thermolyses of Cycloadducts. The identification of **11**, **12**, and **15** suggests that, even during the high-pressure reaction, the fragmentation process had taken place. These observations prompted us to carry out the thermolysis of cycloadducts. When **12** was heated in chlorobenzene at 130 °C for 40 h, **11**, **7b**, and a new compound (**22**) were formed (Scheme 4). The structure of **22** was deduced to be a *retro*-Diels–Alder product of **12**, created by elimination of one furan moiety; the ^{13}C NMR spectrum, showing thirteen lines of signals, indicated this to be a symmetrical molecule. Further thermolysis of **22** in *N*,*N*-dimethylformamide-d_7 in a sealed tube gave **11** and benzene (**23**).

Then, thermolysis of **13b** in a chlorobenzene solution by heating at 130 °C for 43 h gave **14**, the major product, in 40% yield;[3] among others, there were **7b** and a *retro*-Diels–Alder product (**24**) which was supposed to be formed by loss of **7b** and **23** from **13b**. The ^{1}H NMR spectrum of **24** is fully consistent with the structure expressed; i.e., it still retains an oxanor-



Scheme 3.



Scheme 4.

bornene segment, as seen from a characteristically low-field shifted methyl signal (6H, s) at δ=1.56 and an ester methyl signal, δ=3.77. In addition, there is a signal at δ=5.70 (2H, dd, J=7.7 and 2.6 Hz), whose splitting pattern indicated a partial structure of cyclohexadiene. The ^{13}C NMR spectrum of **24** is also informative; the overall signal indicated two overlapping carbon signals, among which, five signals for nine carbons are ascribable to the sp^3-carbons, indicating a pentacarbocyclic skeleton with one ethereal ring.

A quantitative thermolysis of **13b** occurred by heating at 160 °C for 10 h; the thermolysates, **7b**, **23**, and **9** were formed in a ratio of 1.0 : 0.9 : 0.3. The figures are in good accordance with the theoretical, 2 : 2 : 1, from the volatility of the hydrocarbon products. The results of the solid phase thermolysis of **13b** are summarized in Table 2. At 120 °C for 5 h, ca. 50% of **13b** was changed to **14**. For a longer reaction time and at higher temperatures, further fragmentation products (**7b**, **23**, and **24**) were formed (Scheme 5). The results are consistent with *retro*-Diels–Alder fragmentation in a stepwise sequence.

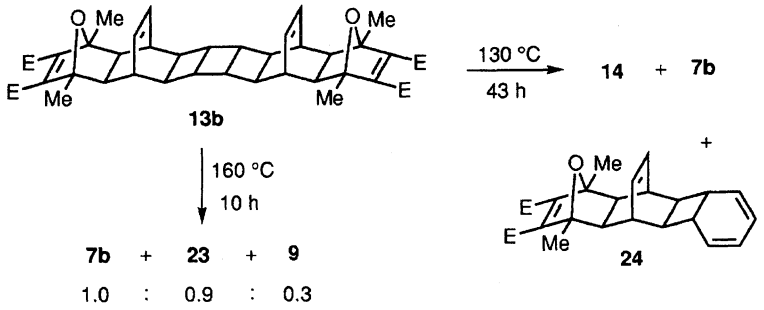
Catalytic hydrogenation of **13b** gave a tetrahydro and an octahydro derivatives (**25** and **26**) (Scheme 6). Orientation of the ester groups of **25** should be *endo*, since the hydrogenation occurred from the convex side of **13b**. Surprisingly, **26** was inert towards cycloreversion; heating in toluene solution at 110 °C for 20 h caused no reaction.

Table 2. Solid Phase Thermolysis of **13b**

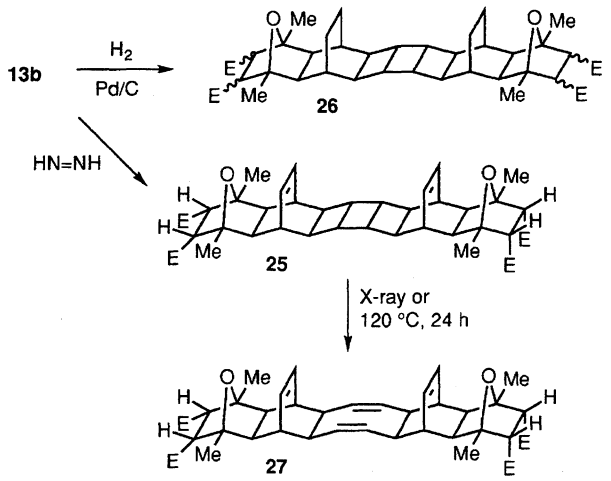
Temperature	Time	Recovered	Products			
°C	h	**13b**	**14**	**7b**	**23**	**24**
120	5	53	46	1	0	0
	19	24	70	4	2	0
	27	0	76	14	10	0
140	1	45	54	1	0	0
	2	3	65	24	8	<1
160	0.16	24	63	11	2	<1

The other *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative, **19**, was thermolyzed, but only dimethyl phthalate (**21**) was identified as a product, other than the recovered material.

The X-Ray Crystallographic Structure Determination of 12. The single crystal of **12** containing two molecules of benzene, obtained by recrystallization from benzene, belongs to the monoclinic system with space group of $P2_1/a$; it contained two molecules in the unit cell. Only a half of the molecule locates at an asymmetric unit. Its cell dimensions were a=10.716 (1),



Scheme 5.



Scheme 6.

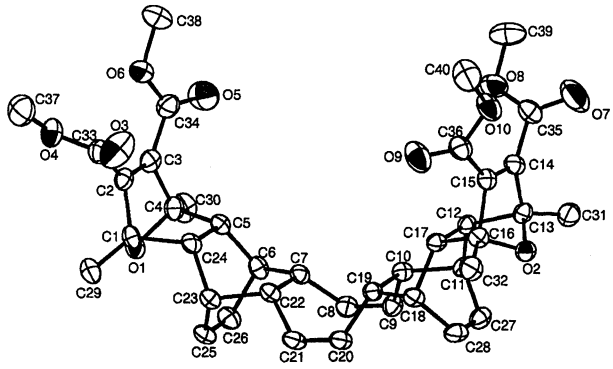


Fig. 2. Perspective view of **14** (=**14-A**).

b=13.903 (1), and c=14.103 (2) Å, with β=97.89 (1)°. The ORTEP diagram of **12** in the final stage, R=0.052, is shown in Fig. 1.

The X-Ray Crystallographic Analyses of 13b and 14. The single crystal of **13b**, obtained by recrystallization from a mixture of cyclohexane and chloroform, initially showed the cell dimensions of a=15.953 (4), b=10.543 (1), and c=26.121 (3) Å, with β=95.66 (1)°. Irradiation with Cu $K\alpha$ line caused a decrease of the monitoring reflection. However, no apparent change of the crystal was detected during the period. This means that a chemical change occurred without disrupting the single crystalline state of **13b**.[8] The final molecular structure solved was equivalent to that of **14** (**14-A**) as shown in Fig. 2. The cell dimensions after exposure to the X-rays were a=15.950 (5), b=10.543 (2), and c=26.370 (6) Å, with β=95.72 (2)°. The change in the cell dimensions throughout the X-ray irradiation was certainly as small as less than 1%. Thus, a single crystal reaction took place.[3,8] Indeed, the ^{1}H NMR spectrum of the sample recovered from the X-ray work was identical with that of authentic **14** and the structure of the compound giving **14** upon X-ray irradiation must be the valence-isomeric **13b**. The X-ray analysis of **14** (**14-B**), whose single crystal was obtained by recrystallization from a mixed solution of cyclohexane and chloroform, independently arrived at the same conclusion; the cell dimensions were a=15.968 (2), b=10.548 (1), c=26.406 (2) Å with β=95.72 (2)°, being slightly larger than those of **14-A**. This means that the **14** formed by single crystalline state reaction with **13b** has a strain to minimize the molecular motion within the lattice. These results were already described in the preliminary communication;[3] the crystal packing is shown in Fig. 3.

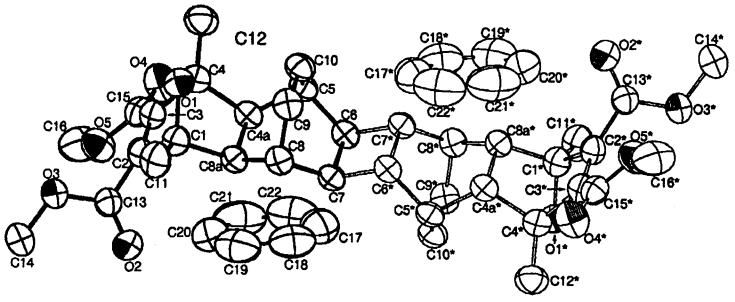


Fig. 1. Perspective view of **12**.

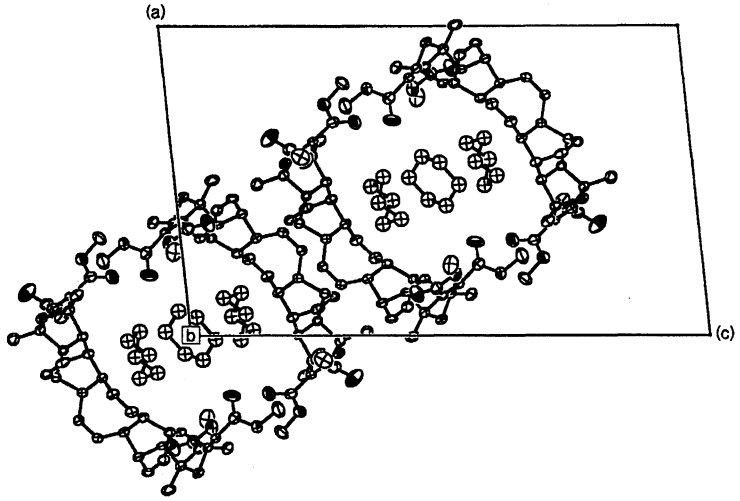


Fig. 3. Molecular packing of **14** along the *b* axis.

However, it is noteworthy that the crystal structures of **14-A** and **14-B** possessed a unique feature; the crystal structures of both **13b** and **14-B** prepared by recrystallization from a mixture of cyclohexane and chloroform provide a spherical space to include solvents in the circular column formed by two hemi-cylindrical molecules.

A tetrahydro derivative (**25**) of **13b** was also exposed to the X-rays for 70 h; the disintegration of the crystalline structure prevented the structure analysis, but, in the ^{1}H NMR spectrum, the sample recovered showed a signal at δ=5.17 (4H, m) that indicates formation of a cyclooctadiene segment in the product (**27**). On the other hand, the crystalline **26**, a mixture of octahydro derivatives, was quite stable toward X-ray radiation.

Thermal Analyses of 13b, 14, and 25. Crystalline **13b**, obtained by recrystallization from a mixture of cyclohexane and chloroform, was analyzed thermogravimetrically; as shown in Fig. 4, 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. This is consistent with the crystallographic analysis. A large mass loss is observed at ca. 182 °C due to *retro*-Diels–Alder reaction as observed in the thermolysis in the solid state. Similar thermal behaviors of **14** are shown in Fig. 5, in which a mass loss of 12.4% due to the elimination of cyclohexane is observed between 104 and 123 °C. On the other hand, the TG (thermogravimetry) of **25** in Fig. 6 showed the larger mass loss of 30.5%, which corresponded to the removal of 3 mol of cyclohexane, at a temperature around 40 °C, lower than **13b** and **14**. Up to 250 °C, no fragmentation was observed. In the DTA (differential thermogravimetric analysis) of **25**, an exothermic peak around 197 °C seemed to be due to the ring opening of the central four membered ring. Although the crystallographic analysis of **25** was unsuccessful because of a lack of the stability towards X-rays, it seemed that **25** also formed a cavity to include cyclohexanes like **13b** and **14**. However, the cavity size of **25** would be large enough to include six cyclohexanes since the four ester groups oriented in the endo direction. Therefore, cyclohexanes were included in **25** more weakly than in **13b** and **14** and they were easily removed to destroy the single crystalline state.

Mechanism of Isomerization. In this re-

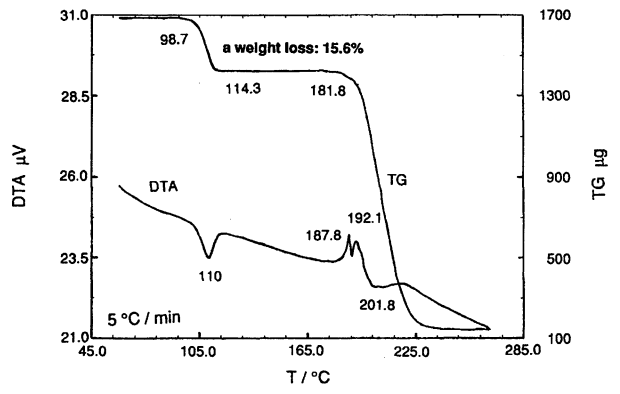


Fig. 4. DTA and TGA thermograms for 3 : 2 cyclohexane complex of **13b** (heating rate 5 °C min^{-1}).

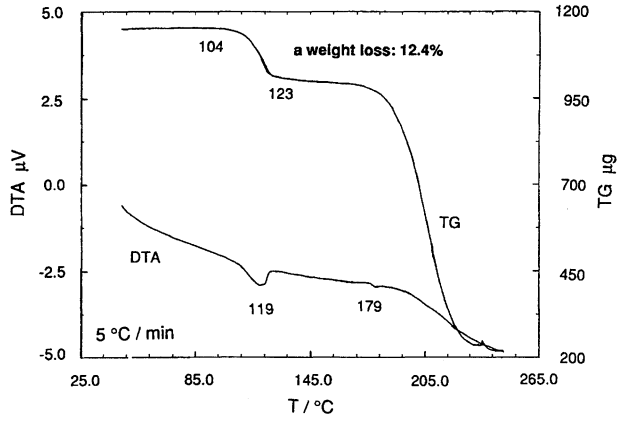


Fig. 5. DTA and TGA thermograms for 3 : 2 cyclohexane complex of **14** (heating rate 5 °C min^{-1}).

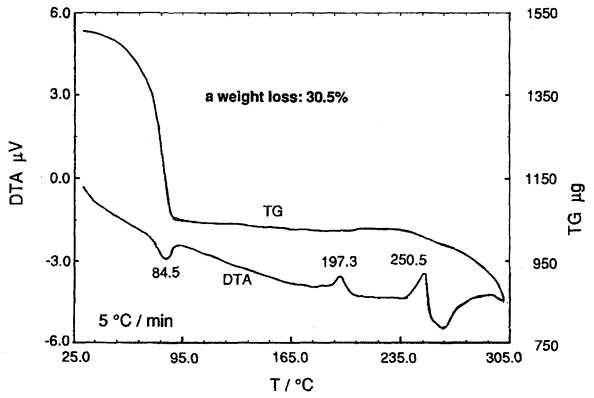


Fig. 6. DTA and TGA thermograms for cyclohexane complex of **25** (heating rate 5 °C min^{-1}).

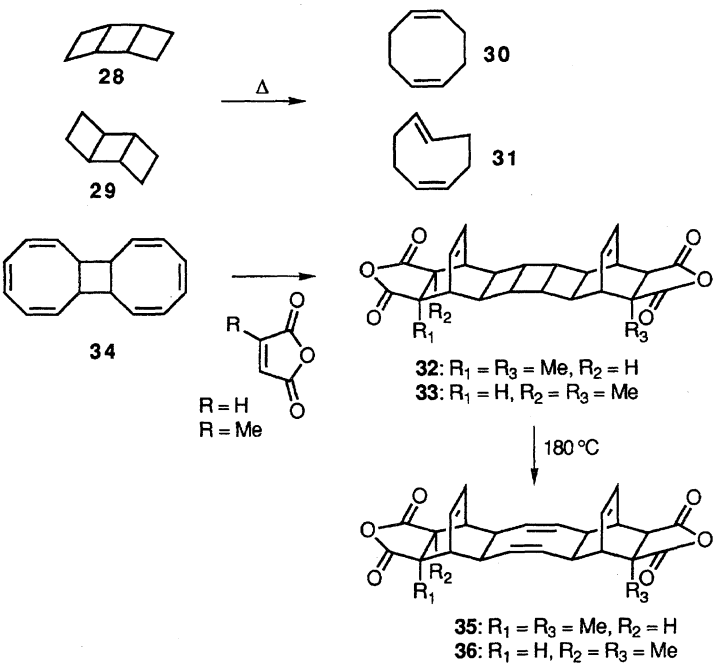
spect, a similar thermal cycloreversion has been observed with *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octanes (**28** and **29**) to *cis,cis*- and *cis,trans*-1,5-cyclooctadiene (**30** and **31**) (Scheme 7).[9] It is true that the similar valence isomerization, tricyclo[4.2.0.0^{2,5}]octanes to 1,5-cyclooctadienes, had occurred in a polycyclic system; bis-Diels–Alder adducts (**32** and **33**) of *syn*-tricyclo-[8.6.0.0^{2,9}]hexadeca-3,5,7,11,13,15-hexaene (**34**) with maleic anhydride and citraconic anhydride gave 1,5-cyclooctadiene derivatives, *retro*-cycloadducts (**35** and **36**).[10] The thermally-allowed valence isomerization, the $[s2\sigma + a2\sigma]$ process, is suggested not to be operative in the constrained molecular structures, and alternatively[10] a stepwise non-concerted process has been proposed. Therefore, the role of the X-ray radiation should be of interest.

The observed parallelism in the results of valence isomerizations under both X-ray and thermal conditions should indicate a similar mechanism. A marked contrast in a behavior towards the X-ray irradiations of a *syn*-tricyclo[4.2.0.0^{2,5}]octane (**13b**) and its octahydro derivative (**26**), which has no π-electrons other than those of carbonyl groups, should, however, indicate a positive role of a π-electron system in the vicinity of the reaction site. This should indicate some electronic effect for the bond cleavage. Thus, occurrence of the reaction **13** to **14** in a single crystalline state, which requires the least molecular motion, firmly ruled out the *antara*-mode involving a concerted process. In the reaction of **13b** to **14**, the X-rays are not simply a heat source of the reaction, but might form a biradical from the strained tricyclo[4.2.0.0^{2,5}]octane system. This should be investigated with appropriately designed molecules.

Conclusion. Thus, the high-pressure Diels–Alder reaction of **9** and **1b** furnished, after dimerization of **9**, a *syn*-tricyclo[4.2.0.0^{2,5}]octane derivative (**13b**). Noteworthy was an occurrence of a rare single crystal reaction, a *retro*-[2+2] cycloaddition, with **13b** to form the valence isomeric cyclooctadiene derivative (**14**) upon exposure to the X-rays. Although the process is thermally disfavored in view of the Woodward–Hoffmann rule, this X-ray facilitated reaction has been realized by thermolysis. At the same time, formation of cavities to include organic compounds by self-ordered arrangement of these half-cylindrical molecules is outstanding. These will be a subject of a forthcoming paper.

Experimental

Elemental analyses were performed by Mrs. R. Hatazoe of this Institute, Kyushu University. The mps were measured with a Yanagimoto Micro mp apparatus and are not corrected. The NMR spectra were measured by JEOL FX 100



Scheme 7.

and GSX 270H spectrometers in $CDCl_3$, unless otherwise specified and the chemical shifts were expressed in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily materials using a JASCO IR-A 102 spectrometer. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

High-Pressure Diels–Alder Reaction of 1b with 9. Formation of Products (10—15). A toluene solution (2 cm^3) of **1b** (200 mg) and **9** (100 mg) was heated at 100 °C under 1000 MPa for 20 h. The mixture was then heated in vacuo to remove the solvent and the residue thus obtained was chromatographed on a silica-gel column to give **10b** [a yellow oil, 63.8 mg; 30%. Found: m/z 446.2095 (M^+). Calcd for $C_{28}H_{30}O_5$: M, 446.2092. ^{1}H NMR δ=1.54 (6H, s), 1.82 (2H, t, J=2.2 Hz), 1.89 (2H, s), 2.16 (2H, m), 2.20 (2H, m), 2.75 (2H, m), 3.71 (2H, m), 3.76 (6H, s), 3.80 (2H, m), 5.68 (1H, t, J=9.3 Hz), 5.88 (1H, t, J=9.3 Hz), and 6.25 (2H, m). ^{13}C NMR δ=15.2 (2C), 28.0 (2C), 34.5 (2C), 35.3 (2C), 43.6 (2C), 48.5 (2C), 52.1 (2C), 79.4—75.9 (4C), 88.3 (2C), 126.0, 126.5, 131.2 (2C), 147.5 (2C), and 164.2 (2C). MS m/z 446 (M^+), 234 (48), 213 (12), 212 (58), 181 (11), 180 (36), 156 (21), 143 (12), 91 (100), and 78 (12)], **11** [a colorless oil, 4.1 mg; 2%. Found: m/z 342.1467 (M^+). Calcd for $C_{20}H_{22}O_5$: M, 342.1466. ^{1}H NMR δ=1.57 (6H, s), 2.03 (2H, s), 2.68 (2H, s), 2.74 (2H, br s), 3.79 (6H, s), 5.82 (2H, s), and 5.91 (2H, m). ^{13}C NMR δ=15.2 (2C), 35.6 (2C), 45.3 (2C), 49.4 (2C), 52.1 (2C), 88.5 (2C), 127.6 (2C), 136.9 (2C), 148.0 (2C), and 164.4 (2C). MS m/z 342 (M^+; 2), 214 (13), 213 (100), 212 (84), 190 (18), 181 (67), 180 (39), 130 (12), and 129 (10)], **12** [colorless prisms, mp 239 °C, 2 mg; <1%. Found: C, 68.42; H, 6.39%. Calcd for $C_{36}H_{40}O_{10}$: C, 68.34; H, 6.37%. ^{1}H NMR δ=1.53 (6H, s), 1.55 (6H, s), 1.74 (4H, s), 1.82 (4H, s), 2.74 (4H, br s), 3.75 (12H, s), and 6.28 (4H, m). ^{13}C NMR δ=15.2 (4C), 34.9 (4C), 41.7 (4C), 48.5 (4C), 52.1 (4C), 88.3 (4C), 132.9 (4C), 147.5 (4C), and 164.2 (4C). MS m/z 632 (M^+; 0.3), 213 (75), 212 (100), 181 (25), 180 (33), and 130 (17)], **13b** [colorless needles, mp 194—195 °C, 83.9 mg; 37%. Found: C, 70.10; H, 6.53. Calcd for $C_{40}H_{44}O_{10}$: C, 70.16; H, 6.48%. ^{1}H NMR δ=1.56 (12H, s), 1.99 (4H, s), 2.27 (4H, s), 2.74 (4H, br s), 2.90 (4H, br s), 3.78 (12H, s), and 6.21 (4H, m). ^{13}C NMR δ=15.2 (4C), 34.9 (4C), 39.2 (4C), 40.8 (4C), 48.5 (4C), 52.1 (4C), 88.4 (4C), 131.3 (4C), 147.5 (4C), and 164.2 (4C). MS m/z 684 (M^+; 0.6), 316 (20), 213 (46), 212 (100), 196 (12), 183 (11), 182 (65), 181 (30), 180 (93), 164 (11), 104 (85), 91 (35), and 78 (58). IR ν 3448, 3040, 2932, 1748, 1719, 1635, 1440, 1383, 1329, 1305, 1257, 1194, 1152, 1107, 1071, 1053, 1026, 918, 882, 846, 798, 741, 702, and 681 cm^{-1}], **14** [colorless needles, mp 187 °C, 4.5 mg; 2%. Found: C, 70.54; H, 6.80%. Calcd for $C_{40}H_{44}O_{10}$: C, 70.16; H, 6.48%. ^{1}H NMR δ=1.55 (12H, s), 2.16 (4H, s), 2.74 (4H, br s), 2.76 (4H, br s), 3.79 (12H, s), 5.22 (4H, s), and 6.26 (4H, m). δ=15.0 (4C), 36.5 (4C), 46.1 (4C), 49.4 (4C), 52.1 (4C), 88.5 (4C), 132.8 (4C), 134.2 (4C), 147.6 (4C), and 164.2 (4C). IR ν 3042, 2984, 2930, 2868, 1719, 1634, 1436, 1383, 1327, 1307, 1258, 1191, 1138, 1107, 1074, 1060, 1030, 917, 889, 872, 815, 795, 759, 727, and 692 cm^{-1}], **15b** (11 mg, 10%), together with recovered **1b** (44 mg).

Thermolysis of 12. A chlorobenzene solution of **12** (38.5 mg) was placed in an autoclave and heated at 130 °C for 40 h. After the solvent was removed in vacuo, the residue thus obtained was chromatographed on a silica-gel column to give **11** (3.3 mg; 29%), **7b**[2] (1.5 mg, 11%) and **22** [a yellow oil, 4.4 mg, 32%. Found: m/z 420.1934 (M^+). Calcd for $C_{26}H_{28}O_5$: M, 420.1935. ^{1}H NMR δ=1.53 (6H, s), 1.55 (4H, s), 1.86 (2H, s), 2.79 (2H, br s), 3.57 (2H, br s), 3.76 (6H, s), 6.23 (4H, m), and 6.42 (2H, m). δ=15.2 (2C), 34.9 (2C), 40.6 (2C), 40.9 (2C), 41.5 (2C), 48.8 (2C), 52.1 (2C), 88.4 (2C), 132.9 (2C), 134.1 (2C), 135.8 (2C), 147.6 (2C), and 164.3 (2C). MS m/z 420 (M^+; 6.7), 214 (10), 213 (89), 212 (100), 190 (18), 182 (10), 181 (91), 180 (91), 130 (32), 129 (48), 128 (13), 115 (23), 91 (15), 78 (12), 52 (47), and 43 (16)], and the recovered **12** (17.8 mg).

Thermolysis of 22. A DMF-d_7 solution (0.3 cm^3) of **22** was sealed and heated on a refluxing toluene bath for 24 h. ^{1}H NMR spectrometry indicated formation of ca. 75% of **11**.

Thermolysis of 13b. A chlorobenzene solution of **13b** (20 mg) was placed in an autoclave and heated at 130 °C for 43 h. After removing the solvent in vacuo, the residue thus obtained was chromatographed on a silica-gel column and HPLC to give **7b** (3.4 mg, 27%), **14** (8 mg, 40%), and **24** [a colorless oil, 2.1 mg, 18%. Found: m/z 394.1769 (M^+). Calcd for $C_{24}H_{26}O_5$: M, 394.1779. ^{1}H NMR δ=1.56 (6H, s), 1.86 (2H, s), 2.34 (2H, br s), 2.42 (2H, br s), 2.87 (2H, br s), 3.77 (6H, s), 5.57 (2H, m), 5.70 (2H, dd, J=7.7, 2.6 Hz), and 6.32 (2H, m). ^{13}C NMR δ=15.2 (2C), 32.8 (2C), 35.1 (2C), 47.9 (2C), 50.5 (2C), 52.1 (2C), 88.4 (2C), 120.7 (2C), 127.6 (2C), 130.7 (2C), 147.4 (2C), and 164.2 (2C). MS m/z 394 (M^+; 1.4), 213 (34), 212 (100), 181 (12), 180 (32), 104 (13), and 78 (11)],

Attempted Photolysis of 13b. A $CDCl_3$ solution (2 cm^3) of **13b** (14.1 mg) was irradiated by means of a low-pressure Hg lamp for 4 h. Monitoring the reaction ^{1}H NMR spectroscopically showed complicated product formations and no further analysis was performed.

Attempted Photolysis of 14. A $CDCl_3$ solution (2 cm^3) of **14** (16.4 mg) was irradiated by means of a low-pressure Hg lamp for 6 h. Monitoring the reaction ^{1}H NMR spectroscopically showed complicated product formations and no further analysis was performed.

High-Pressure Diels–Alder Reaction of 1a with 9. A toluene solution (2 cm^3) of **1a** (211 mg) and **9** (130 mg) was heated at 100 °C under 300 MPa for 20 h. The mixture was then heated in vacuo to remove the solvent and the residue thus obtained was chromatographed on a silica-gel column to give **10a** [a yellow oil, 47.4 mg; 15%. Found: m/z 419.1860 (M+1, FAB-MS). Calcd for $C_{26}H_{27}O_5$: M, 419.1858. ^{1}H NMR δ=1.82—1.88 (4H, m), 2.10 (2H, br s), 2.25 (2H, br s), 2.79 (2H, br s), 3.70 (2H, m), 3.78 (6H, s), 3.82 (2H, m), 4.89 (2H, s), 5.67 (1H, t, J=9.5 Hz), 5.88 (1H, t, J=9.5 Hz), and 6.21 (2H, m). ^{13}C NMR δ=28.0 (2C), 35.3 (2C), 36.6 (2C), 43.0 (2C), 44.1 (2C), 52.2 (2C), 74.5—76.2 (4C), 84.1 (2C), 126.0, 126.5, 131.5 (2C), 144.5 (2C), and 163.2 (2C). MS m/z 418 (M^+; 8), 156 (12), and 91 (100)], **17** [a pale yellow oil (lit,[5] mp 118—120 °C), 9.9 mg; 4%. ^{1}H NMR δ=1.94 (4H, m), 2.20 (2H, br s), 3.76 (6H, s), 3.80 (4H, br s), 4.00 (2H, br s), 5.70 (1H, t, J=9.5 Hz), 5.84 (1H, t, J=9.5 Hz), and 6.45 (2H, m). ^{13}C NMR δ=27.8 (2C), 33.3 (2C), 42.7 (2C), 42.8 (2C), 52.1 (2C), 77.0 (4C), 126.1, 126.7, 133.3 (2C), 141.8 (2C), and 166.6 (2C). MS m/z 350 (M^+;

19), 163 (23), 156 (14), 155 (12), 141 (12), 129 (18), 128 (17), 115 (17), 91 (100), and 77 (11)], **13a** [colorless needles, mp 171 °C, 6.4 mg; 1%. Found: *m/z* 629.2390 (M+1, FAB-MS). Calcd for $C_{36}H_{37}O_{10}$: M, 629.2387. ^{1}H NMR δ=1.95 (4H, s), 2.25 (4H, s), 2.78 (4H, br s), 2.96 (4H, s), 3.80 (12H, s), 4.92 (4H, s), and 6.17 (4H, m). MS *m/z* 628 (M^+; 0.5), 224 (10), 197 (24), 186 (10), 185 (13), 184 (41), 182 (18), 154 (10), 153 (100), 150 (10), 104 (97), 91 (25), and 78 (82)] and **15a** (3.6 mg, 2%), together with recovered **1a** (31 mg).

Reduction of 13b with Diimide. Formation of Tetrahydro Derivative (25). To a CH_2Cl_2 solution (5 cm^3) of **13b** (100 mg) and $K_2(NCO_2)_2$ (310 mg) was added AcOH (438 mg) at −10 °C and this mixture was stirred for 3 h. It was then neutralized with $NaHCO_3$ and extracted with CH_2Cl_2 to give **25** [colorless needles, mp 263 °C, 100 mg, 100%. Found: C, 69.02; H, 6.92%. Calcd for $C_{40}H_{48}O_{10}\cdot 1/4H_2O$: C, 69.29; H, 7.05%. ^{1}H NMR δ=1.45 (12H, s), 2.20 (4H, s), 2.45 (4H, s), 2.60 (4H, br s), 2.90 (4H, br s), 2.91 (4H, s), 3.72 (12H, s), and 6.22 (4H, m). ^{13}C NMR δ=18.4 (4C), 34.7 (4C), 40.0 (4C), 40.3 (4C), 46.4 (4C), 51.7 (4C), 56.2 (4C), 87.1 (4C), 131.8 (4C), and 171.3 (4C)].

Catalytic Reduction of 13b. Formation of Octahydro Derivative. A mixed solution of MeOH (5 cm^3) and EtOAc (5 cm^3) of **13b** (112 mg) was reduced with Pd/carbon at room temperature under 0.4 MPa for 12 h. The product obtained was a stereoisomeric mixture of **26**.

Thermolysis of 25. Formation of 27. Crystalline **25** (20 mg) was placed in a sealed glass tube and heated at 120 °C for 24 h. A colorless oil obtained was **27** [6.7 mg, 33%. δ=1.43 (12H, s), 2.60 (8H, s), 2.79 (4H, s), 2.91 (4H, s), 3.71 (12H, s), 5.16 (4H, s), and 7.28 (4H, m)].

Attempted Thermolysis of 26. Crystalline **26** (3 mg) was similarly placed in a sealed glass tube and heated at 180 °C for 20 h. The NMR spectrometry indicated a quantitative recovery of the starting material.

High-Pressure Diels–Alder Reaction of 3 with 9. A toluene solution (4 cm^3) of **3** (1.37 g) and **9** (1.01 g) was heated at 70 °C under 300 MPa for 20 h. After removing the solvent, the residue was chromatographed on a silica-gel column to give **17** (a colorless oil, 526 mg, 16%),[5] **18** (a colorless oil, 739 mg, 31%),[7] **21** (dimethyl phthalate, a colorless oil, 117 mg, 6%), **19** [colorless needles, mp 172—173 °C (lit,[6] mp 162—163 °C), 222 mg, 10%. ^{1}H NMR δ=2.13 (4H, s), 2.85 (4H, br s), 3.77 (12H, s), 4.01 (4H, m), and 6.39 (4H, m). ^{13}C NMR δ=36.2 (4C), 40.6 (4C), 42.8 (4C), 52.2 (4C), 133.2 (4C), 142.1 (4C), and 166.5 (4C)] and **20** [colorless prisms, mp 204 °C (lit,[5] mp 196—198 °C), 139 mg, 7%. δ=1.71 (4H, s), 3.75 (12H, s), 4.04 (4H, m), and 6.49 (4H, m). ^{13}C NMR δ=40.9 (4C), 42.7 (4C), 52.2 (4C), 135.4 (4C), 142.6 (4C), and 166.4 (4C)].

Thermolysis of a Mixture of 19 and 20. A mixture of **19** and **20** (8 : 2) in a sealed glass tube was heated at 120 °C for 30 h. After the solvent was removed, the residue thus obtained was chromatographed on a silica-gel column to afford dimethyl phthalate (21%), together with **19** (52%) and **20** (27%). No valence isomer was detected.

X-Ray Crystallography. Data collection was performed with Cu $K\alpha$ radiations on an Enraf–Nonius FR 590 computer controlled equipment. Structures were solved by direct method (SIR88)[11] and differential Fourier syntheses. Reflections having intensities greater than 3.0 times their standard deviation were used to refine the structures in full matrix least squares. The positions of hydrogen atoms of **12** and those of **13b** and **14**, except those of the ester methyls, are refined with fixed isotropic thermal factors (4.0 Å^2). Hydrogen atoms on the ester methyls of **13b** and **14** and cyclohexanes were included in the refinements, but restrained to ride on the carbon atoms to which they are bonded. Those isotropic thermal factors are fixed at 1.3 times of those of the corresponding carbon atoms. Atomic scattering factors were adopted from an international data book.[12] The highest peak in the final difference Fourier had a height of 0.19 e Å^{-3} for **12**, 0.51 e Å^{-3} for **13b**, 0.34 e Å^{-3} for **14** and the minimum negative peak had a height of −0.38 e Å^{-3} for **12**, −0.23 e Å^{-3} for **13b**, −0.12 e Å^{-3} for **14**. All calculations were performed on a Micro Vax 3100 computer

Table 3. Crystal Data and Conditions of Measurements

	12	**13b (=14-A)**	**14-B**
Molecular formula	$C_{48}H_{52}O_{10}$	$C_{59}H_{62}O_{10}$	$C_{59}H_{62}O_{10}$
Molecular weight	788.94	811.03	811.03
Crystal dimension/mm	0.30×0.2×0.15	0.4×0.3×0.2	0.30×0.20×0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/n$	$P2_1/n$,
a/Å	10.716(1)	15.953(4)	15.969(2)
b/Å	13.903(1)	10.543(1)	10.548(1)
c/Å	14.103(2)	26.181(3)	26.406(2)
β/°	97.89(1)	95.66(1)	95.720(9)
V/Å^3	2081.4(4)	4382(1)	4425.4(9)
Z	2	4	4
D_c/g cm^{-3}	1.26	1.22	1.22
Scan type	ω–2θ	ω–2θ	ω–2θ
$2\theta_{max}$/°	130	130	130
No. of reflections measured	3451	7461	7530
No. of reflections observed [$I \geqq 3\sigma(I)$]	2602	3952	3495
R	0.052	0.110	0.070
wR	0.072	0.127	0.084

using MolEN (An Interactive Structure Solution Procedure, Enraf–Nonius, Delft, The Netherlands (1990)). Fundamental crystal data and conditions of measurements are compiled in Table 3.[13)]

The work was partially supported by a Grant-in-Aid for Scientific Research No. 06242215 to A. M. from the Ministry of Education, Science and Culture.

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