and thermal decomposition of I<sub>2</sub>, followed by I atom reaction with 0,

$$I_2 + M \rightleftharpoons 2I + M \tag{12}$$

$$I + O_3 \rightarrow \text{products}$$
 (13)

Thermal decomposition of O<sub>3</sub> is too slow in this temperature range to account for the observed reaction rates. The activation energy for the forward step of reaction 10 is 103 kJ·mol<sup>-1,13</sup> According to the data of Benson and Axworthy,<sup>13</sup> for the reaction times used in our work, about 0.01% of the initial O3 would have reacted at 293 K and about 7% at 370 K. Reaction via the thermal decomposition of I<sub>2</sub> would be even slower, in the absence of light, because an activation energy equal to or greater than the bond dissociation energy of  $I_2$  (151 kJ·mol<sup>-1</sup>) would be required. Thus, atomic reaction mechanisms cannot account for the observed rate data.

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# 4. Conclusions

Elemental iodine was shown to react with ozone, forming a solid iodine oxide with the stoichiometric composition  $I_4O_9$ . The stoichiometry, rate, and temperature dependence of this reaction were studied in the range 293-370 K. The observed kinetics suggest that the rate-determining step is a bimolecular reaction between I<sub>2</sub> and O<sub>3</sub> to form I, IO, and IO<sub>2</sub> radicals, which undergo further oxidation by reaction with  $O_3$  to form the final  $I_4O_9$ product.

The reaction rate and product stability are suitable for application of this reaction to the removal of radioactive iodines from air in nuclear facilities. In the presence of ionizing radiation, such as in a nuclear reactor accident, where some ozone would be produced by radiolytic decomposition of the oxygen in the air, the reaction of  $I_2$  with  $O_3$  is expected to reduce the potential releases of volatile radioiodines.

Acknowledgment. We thank Ms. D. A. Furst and Mr. B. D. Wilson for their assistance and Drs. D. F. Torgerson and P. Taylor for helpful discussions.

Registry No. I<sub>2</sub>, 7553-56-2; O<sub>3</sub>, 10028-15-6.

# Photoinduced Isomerization of Radical Ions. 3. Radical Cations of Cyclopentadiene, Dicyclopentadlenes, and 1,3-Bishomocubane Produced in $\gamma$ -Irradiated Freon Matrices at 77 K

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The radical cations of cyclopentadiene and the three  $C_{10}H_{12}$  systems in the title have been produced in  $\gamma$ -irradiated Freon matrices at 77 K. Electronic and ESR spectroscopy were used to determine the interrelationships among the cations and their photoproducts. The three  $C_{10}H_{12}^{+}$ 's yielded different photoproducts depending upon the wavelength used for photoexcitation. The photoproduct obtained from endo-dicyclopentadiene cation excited to its first excited state was also obtained by a thermal reaction between the neutral molecule of cyclopentadiene and its radical cation. The product is inferred to be the radical cation of a new dicyclopentadiene. Possible mechanisms of obtaining this new  $C_{10}H_{12}^{+}$  isomer are discussed.

#### 1. Introduction

 $\gamma$ -Irradiation of frozen solutions using Freons as the solvent leads to the production of solute radical cations.1 A glass-forming admixture of CCl<sub>3</sub>F and CF<sub>2</sub>BrCF<sub>2</sub>Br (1:1 by volume) is used for the optical studies because of its transparency in the near-UV and near-IR regions.<sup>2-4</sup> For the ESR study a polycrystalline matrix of CCl<sub>3</sub>F is found useful.<sup>1,5</sup> In this serial work we present the result of studies on the radical cations in the title as well as that of trans-tricyclo[3.0.3.0]deca-2,8-diene. They were produced by irradiation in the Freon mixture mentioned above (abbreviated as FM hereafter). In a separate paper we have discussed the nature of the electronic absorption spectra of the radical cations of endo- and exo-dicyclopentadienes in FM.6 In the present paper

our focus will be mainly on the spectral change induced upon photoexcitation.

The dependence of the optical spectrum upon the initial concentration of cyclopentadiene was also examined. Subsidiary ESR studies were carried out briefly. Complete identification of all the photoproducts was not achieved owing to the complexity of the system. However, the photoinduced reactions are consistently interrelated and plausible reaction mechanisms are considered (see Scheme I).

#### 2. Experimental Section

endo-Dicyclopentadiene was commercially obtained. Cyclopentadiene was produced therefrom by the standard method. exo-Dicyclopentadiene and 1,3-bishomocubane were synthesized and isolated by literature procedures.<sup>7,8</sup> A less stable dicyclopentadiene, trans-tricyclo[3.0.3.0]deca-2,8-diene, was also synthesized as an admixture with endo- and exo-DCP.9,10

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**Figure 1.** Optical spectra of irradiated cyclopentadiene in FM at 77 K. Curves 1a-1e correspond to the initial concentration of 1/1000, 1/500, 1/100, 1/50, and 1/20 by volume ratio. The peaks denoted by the upward open arrows are attributed to the radical cation of cyclopentadiene monomer. Curve 1f was obtained upon photobleach of the sample of curve 1e with  $\lambda \gtrsim 690$  nm. The eliminated band at 825 nm is assigned to a  $\pi$  dimer cation (route M in Scheme I).

The hydrocarbons were dissolved to a concentration of 1/1000 to 1/20 by volume in FM as described previously.<sup>4</sup> The degassed solutions were frozen to a glassy solid at 77 K in a 1.5 mm thick optical cell or in a 3-mm ESR tube and irradiated at 77 K. The radiation dose was in the range of  $10-10^2$  Gy (Gy = J kg<sup>-1</sup> in SI units) to obtain optical densities of the radical cations up to about 2. A Cary 17I spectrophotometer and a JEOL-PE3X ESR spectrometer were used. All the optical spectra in Figures 1-8 were plotted by subtracting the "background" absorption of samples before irradiation, so that the spectra are attributable to the species produced upon irradiation. Samples after irradiation were photobleached by using Toshiba glass filters and a projector lamp.

The mechanism of the radical cation formation in irradiated FM matrices is described elsewhere.<sup>1</sup> Briefly, irradiation produces positive holes and electrons in the matrix; the former are transferred intermolecularly to solute hydrocarbons to produce their cations. The conversion from the neutral solute molecule to its cation is  $\gtrsim 1\%$  under the condition of the irradiation.

#### 3. Results

(1) Cyclopentadiene. Figure 1a-e shows the spectra of irradiated cyclopentadiene in FM with the initial concentration of the diene being increased from 1/1000 to 1/20 by volume ratio. The broken curve at the bottom indicates an estimated absorption due to matrix-originating neutral radicals such as  $\cdot CF_2CF_2Br$ produced concomitantly upon irradiation.<sup>4e</sup> All the spectra in Figure 1 comprise this unwanted absorption. The rest of the absorptions in Figure 1a are attributed to the radical cation of



**Figure 2.** Optical spectra of irradiated *endo*-dicyclopentadiene in FM at 77 K. Upper: The spectrum is attributed to the radical cation of *endo*-DCP in the bis-cyclopentaallylic structure.<sup>6</sup> Lower: Same as above after photobleach with  $\lambda = 620-1000$  nm for 20 min. The spectrum is tentatively attributed to the radical cation of a new DCP with a  $C_{2h}$  symmetry (species 6 in Chart I). The photochemical change corresponds to route A in Scheme I.

cyclopentadiene. The structured bands at 612-509 and 368-343 nm are attributed to the first and second  $\pi$  electron transitions,  $1^2A_2 \rightarrow 1^2B_1$  and  $1^2A_2 \rightarrow 2^2B_1$ , respectively.

As the initial concentration exceeds 1/1000, the spectrum after irradiation changed gradually as shown in Figure 1b-e; i.e., the absorption of the cyclopentadiene cation decreased and new absorptions appeared at 1800, 825, 410, and 393 nm. The absorption at 825 nm and the ones at 1800, 410, and 393 nm behaved differently; i.e., the 825-nm band was eliminated by photolysis of the sample with  $\lambda \gtrsim 690$  nm light (filter R69) as shown in Figure 1f (dotted curve). Close examination of Figure 1, e and f, reveals that the absorption at 612-509 and 368-343 nm increased slightly upon photobleaching the 825 nm.

(2) endo-Dicyclopentadiene. Upon irradiation of endo-DCP in FM (1/200 by volume), the spectrum in Figure 2(upper) was obtained. The spectrum is attributed to the radical cation of endo-DCP whose conformation is of a bis-cyclopentaallylic type.<sup>6</sup>

The spectrum in Figure 2 does not have an absorption at 825 nm nor absorptions at 1800, 410, and 393 nm. Therefore, it can be ruled out that some of the cyclopentadiene molecules dimerized to *endo*-DCP before irradiation in the above experiment of the cyclopentadiene system.

It was found, however, that the spectrum in Figure 2(upper) changes easily to that in Figure 2(lower) upon photobleaching with  $\lambda = 620-1000$  nm (filters R62 + IRA25S, 20 min). The wavelengths correspond to the broad band with  $\lambda_{max} = 743$  nm in Figure 2(upper). The lower spectrum in Figure 2 is comparable with the spectrum in Figure 1f. In Figure 1f, residual absorptions due to the cyclopentadiene cation are seen at 612-509 nm and at 369-343 nm. When these absorptions are subtracted from the spectrum in Figure 1f, the result is almost identical with that in Figure 2(lower). It is emphasized that the slight vibrational

Scheme I. Correlations among the Various  $C_{10}H_{12}^{+}$  Systems and the Cyclopentadiene Radical Cation<sup>a</sup>



<sup>a</sup> The numbers in the rectangles indicate  $\lambda_{max}$  in nanometers. The numbers beside the alphabetic symbols denote the wavelengths in nanometers used for the photobleach. The open arrows indicate dimerizations. Possible rearrangements and structures are indicated in parentheses.

structure upon the 1800-nm band is definite and reproducible. The observed spectral change from the upper to the lower part of Figure 2 will be discussed in connection with route A in Scheme I.

The spectrum in Figure 2(lower) did not change on prolonged illumination with  $\lambda = 620-1000$  nm. However, with shorter wavelengths corresponding to the absorptions at 410, 393, and 378 nm in Figure 2(lower) ( $\lambda = 300-500$  nm, filter V40), complicated spectral changes were observed as shown in Figure 3: (i) The initial absorption at 1800 nm decreased in parallel with the absorptions at 410 and 393 nm as the downward arrows indicate. (ii) In the middle stage of illumination an increase followed by a decrease was observed at 743 nm. Although not distinct, parallel changes were noted at 401 and 385 nm. (iii) Later on, absorptions at around 531 nm increased as the upward arrows indicate. Very weak structured absorptions at about 700-1000 nm accompanied the absorptions at about 531 nm. (iv) Although not quite apparent in Figure 3, another rise and decay is considered to proceed at about 1700 nm in reference to the result of Figure 4 (see below). (v) In the near-UV region two peaks at 369 and 354 nm increased with illumination uniformly.

The spectral change of i implies that the absorptions at 1800, 410, 393, and 378 nm are due to a common, absorbing species. For convenience we call the whole absorption in Figure 2(lower) the " $1.8\mu$  band". The changes of i-iv above imply that the species giving the  $1.8\mu$  band is first subject to a "back-reaction" to reproduce the *endo*-DCP cation, absorbing at 743, 401, and 385 nm (route B in Scheme I), and then prolonged illumination of the reproduced *endo*-DCP cation eventually gives species responsible for the absorptions at about 531 nm plus weak structured absorptions at about 700-1000 nm (routes C and D in Scheme



Figure 3. Spectral changes upon photobleaching of the species giving spectrum in Figure 2(lower) with  $\lambda = 300-500$  nm. The changes are associated with routes B  $\rightarrow C \rightarrow D$  and routes E and F in Scheme I.

I). The presumed intermediacy of species associated with the  $1.7\mu$  band in Scheme I is necessary to be consistent with the later experiments. The absorptions at 369 and 354 nm appearing in v are comparable with the absorptions at 368 and 354 nm in Figure 1a. They are regarded as due to the radical cation of cyclopentadiene produced by a route B followed by route E in Scheme I. The slight spectral shift from 368 to 369 nm may be ascribed to a possible perturbation by neighboring molecules (route F is





Figure 4. Spectral changes upon photobleaching of the *endo*-DCP cation with  $\lambda = 300-500$  nm. The changes are associated with route C  $\rightarrow$  D and route E in Scheme I.



Figure 5. Optical spectra of irradiated *exo*-DCP in FM at 77 K, and the spectral changes after successive photobleachings with  $\lambda = 610-1000$  nm. Bold curve: spectrum immediately after irradiation. It is attributed to the radical cation of *exo*-DCP in the bis-cyclopentaallylic form.<sup>6</sup> The spectral changes upon photobleach are associated with route G in Scheme I.

also conceivable although the efficiency of this direct path seems not to be large).

Figure 4 demonstrates spectral changes on illumination of the endo-DCP cation with  $\lambda = 300-500$  nm (filter V40): (i) the initial absorptions at 743, 401, and 385 nm decreased as the downward arrows indicate; (ii) in the middle stage of illumination a broad band with  $\lambda_{max} \simeq 1700$  nm first increased and then diminished; (iii) the diminution was accompanied with the appearance of several absorptions at about 500-550 nm and very weak structured absorptions at about 500-550 nm and very weak structured absorptions at about 500-550 nm end very weak structured absorptions at about 500-1000 nm (see, e.g., the minute peak at 802 nm); (iv) the absorptions in the near-UV region with  $\lambda_{max} = 369$  and 354 nm increased in proportion to the decrease in the absorptions at 743, 401, and 385 nm. The spectral changes shown in Figure 4 are essentially similar to those observed in the later stage of Figure 3. The spectral changes of i-iii are related below to routes C and D, and the change iv is related to a parallel route E in Scheme I.

(3) exo-Dicyclopentadiene. Figure 5 illustrates the absorption of irradiated exo-DCP in FM. The bold curve represents the spectrum immediately after irradiation and is attributed to the radical cation of exo-DCP whose conformation is also regarded as a bis-cyclopentaallylic type.<sup>6</sup> Similar to the spectrum of the



Figure 6. Spectral changes upon photobleaching of the *exo*-DCP cation with  $\lambda = 300-500$  nm. The changes are associated with route  $G \rightarrow D$  and routes H and I in Scheme I.



Figure 7. Optical spectra of irradiated 1,3-bishomocubane in FM at 77 K, and the spectral change after photobleach with  $\lambda \gtrsim 1000$  nm. Bold curve: Spectrum immediately after irradiation. The monotonous absorption in the broken curve is attributed to the radical cation of 1,3-bishomocubane. It is superimposed with the absorption due to the *endo*-DCP cation. Fine curve: Same as above after photobleach with  $\lambda \gtrsim 1000$  nm. The change is associated with route J in Scheme I.

endo-DCP cation in Figure 2(upper), the first band appears in the near-IR and is broad. The second band appears in the near-UV, although the vibrational structure of the latter is less pronounced compared with that in Figure 2(upper).

In remarkable contrast to the *endo*-DCP cation, photobleaching with  $\lambda = 610-1000$  nm (filters R61 + IRA25S) did not give the 1.8 $\mu$  band, but the initial spectrum, in bold curve, merely changed slowly as the family of curves in Figure 5 demonstrate. Close examination reveals that the 1.7 $\mu$  band is probably produced (route G in Scheme I). Also, weak and broad absorptions seem to appear throughout the whole spectral region to compensate the decrease of the initial absorption with  $\lambda_{max} = 850$  and 392 nm (see upward arrows).

Figure 6 shows the result of photolysis of the *exo*-DCP cation with  $\lambda = 300-500$  nm (V40): (i) In the early stage the  $1.7\mu$  band appears as in Figure 5 (route G). Also, the appearance of the *endo*-DCP cation is noted by the small peak at 401 nm and the gradual shift of the broad and of  $\lambda_{max} = 850$  nm toward 743 nm (see the tilted arrow) (route H in Scheme I). (ii) Later, the *endo*-DCP cation starts to decrease, and the absorptions at about 450-650 nm as well as the minute ones at about 700-1000 nm



Figure 8. Spectral changes upon photobleaching of the 1,3-bishomocubane cation. Upper: After photobleach with  $\lambda \gtrsim 690$  nm. The change is associated with route J  $\rightarrow$  A and route K. Lower: After succeeding photobleach with  $\lambda = 440-600$  nm. The change is associated with route L in Scheme I.

appear in consistence with the result of Figure 4 (routes C and D in Scheme I). The relatively uniform increase in the absorption at 369 and 354 nm is similar to the spectral change in Figure 4 which requires the assumption of route I in parallel with routes G and H.

(4) 1,3-Bishomocubane. Irradiation of 1,3-bishomocubane in FM yielded the spectrum given as the solid bold curve of Figure 7. The broad, featureless absorption indicated by the broken curve is regarded as due to the radical cation of 1,3-bishomocubane (see Discussion). It is apparent that some of the 1,3-bishomocubane cations have changed to *endo*-DCP cations, even immediately after irradiation (cf. Figure 2(upper) and the solid bold curve of Figure 7).

Although the absorption spectrum in broken curve is featureless, photochemical effects depend upon the wavelengths used for illumination; the fine curve in Figure 7 demonstrates the effect of photolysis with wavelengths near the red edge of the absorption spectrum ( $\lambda \gtrsim 1000$  nm, filter IRD80B). It indicates partial conversion of 1,3-bishomocubane cations to the *endo*-DCP cations (route J). The slight appearance of the 1.8 $\mu$  band may be due to the subsequent conversion corresponding to route A in Scheme I.

However, when irradiated 1,3-bishomocubane systems were first bleached with slightly shorter wavelengths,  $\lambda \gtrsim 690$  nm (filter R61 or R65 or R69), the conversion to the 1.8 $\mu$  band proceeded efficiently as shown in Figure 8(upper) (routes J and A with  $\lambda \gtrsim 690$  nm). In addition, new absorptions at 592, 535, and 487 nm are seen in Figure 8(upper) (route K in Scheme I). Subsequent photolysis with  $\lambda = 440-600$  nm (filters B46 + Y44), which covers the new absorptions, for a brief period (about 5 min) caused a remarkable spectral change as shown in Figure 8(lower). The sharp absorptions peaking at, e.g., 531 nm and at about 700-1000 nm are in common with those in Figures 3 and 4. The change is associated with route L. During the photolysis with  $\lambda = 440-600$  nm, the  $1.8\mu$  band remained unchanged. Apparently, the wavelengths of 440-600 nm are too long to induce the second transition corresponding to the absorptions at 410, 393, and 378 nm of the  $1.8\mu$  band. Also, the absorptions at 369 and 354 nm observed in Figures 3 and 4 (routes E and F) do not appear in Figure 8(lower), correlating with the decreased photon energy of  $\lambda = 440-600$  nm.

(5) trans-Tricyclo[3.0.3.0]deca-2,8-diene. In an attempt to identify the species giving the  $1.8\mu$  band we synthesized the hydrocarbon in the above subtitle (species 1 in Chart I). However, only a mixture of the hydrocarbon contaminated with the two DCP and cyclopentadiene was obtained, and we failed to isolate the hydrocarbon alone. Thus, we employed the mixture in the FM matrix radiolysis expecting to observe superposing spectra of the radical cations of all the components. However, the resulting spectrum indicated only the formation of the radical cations of the endo- and exo-DCP's and cyclopentadiene. The result suggests that the radical cation of trans-tricyclo[3.0.3.0]deca-2,8-diene is not stable in the FM matrix at 77 K and that the  $1.8\mu$  band is not related to this hydrocarbon.

(6) ESR Spectra of endo- and exo-Dicyclopentadienes and 1,3-Bishomocubane. The ESR spectra of the radical cations of endo- and exo-DCP's corresponding to the samples giving the spectra in Figure 2(upper) and Figure 6 (bold curve) are broad singlets with a peak-to-peak width of 31 and 15 G, respectively. These spectra show only that the optical spectra are associated with the paramagnetic radical cations of the respective dicyclopentadienes. In parallel with the optical change from the upper to the lower spectrum in Figure 2 the ESR singlet changed slightly in the line shape. The ESR spectrum of the radical cation of 1,3-bishomocubane is a slightly asymmetric quintet with a total bandwidth of about 90 G.

# 4. Discussion

(1) Cyclopentadiene. As mentioned in section 3.1, the spectrum in Figure 1a is attributed to the radical cation of monomeric cyclopentadiene (M). The prototype butadiene also exhibits similar absorptions when its FM solutions are irradiated at 77 K.<sup>11</sup> At the highest concentration three absorbing species are produced (Figure 1e). One is the residual M<sup>+</sup>, the second species is responsible for the 825-nm band, and the third one for the  $1.8\mu$ band. In concentrated solutions some of the solute molecules M may have been frozen as neutral dimers M···M before irradiation. By analogy with the broad absorption band of  $\pi$  dimer cations of olefins<sup>12</sup> the 825-nm band in Figure 1e is tentatively assigned to a similar sandwich type  $\pi$  dimer cation of cyclopentadiene (route M).

As repeatedly shown (Figures 1f, 2, 3, and 8) the absorption at 1800 nm behaves in parallel with those at 410, 393, and 378 nm. Therefore, all these absorptions are associated with a common species. The near-IR band at 1800 nm is vibrationally structured, which suggests a fairly rigid molecular structure for the species responsible for the absorption. Such a structured band has not been known for sandwich type  $\pi$  dimer cations. Since the 1.8 $\mu$ band is obtained both from the photolysis of the *endo*-DCP cation (Figure 2, lower) and from the thermal reaction between M and M<sup>+</sup> (route N), it seems reasonable to associate the absorption with the radical cation of a C<sub>10</sub>H<sub>12</sub> system with a molecular conformation different from both *endo*- and *exo*-DCP.

The fact that we have both the 825-nm band and the  $1.8\mu$  band in Figure 1e suggests that some of the neutral dimers of cyclopentadiene in the frozen matrix are in an orientation suitable for the assumed reaction,  $M + M^+ \rightarrow C_{10}H_{12}^+$ , whereas the rest are in a different orientation giving only sandwich type  $\pi$  dimer cations. The spectral change from Figure 1e to 1f, i.e., the disappearance of the 825-nm band and the slight increase of the absorptions of  $M^+$ , may be accounted for if we assume that

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Chart I



photoexcitation of the  $\pi$  dimer cations causes the dissociation into M and M<sup>+</sup> (route O).

In order to identify the  $C_{10}H_{12}^+$ , produced by the above reaction, we had recourse to the SOMO-HOMO interaction in the reaction of  $M + M^+$ . Plausible, thermally allowed reactions to produce the  $C_{10}H_{12}^+$  are  $(\pi 2 + \pi 2)$ ,  $(\pi 4 + \pi 4)$ , and  $2 \times (\pi 2 + \pi 2)$ interactions which should yield 1-4, 5 and 6, and 7 and 8 in Chart I. Since the radical cations of 7 and 8 are expected to exhibit featureless spectra by analogy with those of 1,3-bishomocubane (Figure 7, broken curve) and a number of saturated hydrocarbons,<sup>13</sup> the possibility of 7 and 8 may be ruled out. There seems to be no report of synthesis of 3-6, but 1 and 2 have been synthesized.<sup>9,10</sup> As described in section 3.5, the possibility that 1 is related to the  $1.8\mu$  band seems slim. By inference we conjecture that 1-4, all having a strained four-membered ring, are not related to the  $1.8\mu$  band. Thus, 5 and 6 remain as candidates if the above reaction mechanism is operative, although 6 would be more favorable in view of steric hindrance. If not, however, we can only conclude that the  $1.8\mu$  band is related in all probability to a DCP whose conformation is different from those associated with endoand exo-DCP.6

(2) endo- and exo-Dicyclopentadienes. The broad absorption bands was  $\lambda_{max} = 743$  nm (Figure 2, upper) and 850 nm (Figure 5, bold curve) for the two DCP cations might be regarded as the intramolecular charge-transfer bands involving the two ethylenic units. However, reference to the photoelectron spectra of the two DCP's and MO calculations<sup>6</sup> indicates that the nascent radical cations of the DCP's isomerize to bis-cyclopentaallylic radical cations which retain largely the "endo" and the "exo" characters of the nascent radical cations as illustrated in the respective frames of Scheme I. The absorption bands have been associated with the charge-resonance type interaction between the two fivemembered rings.<sup>6,14</sup> The fact that the 1.8 $\mu$  band can be obtained from the endo-DCP cation but not from the exo cation may be understood by considering the geometrical difference between the two bis-cyclopentaallylic radical cations shown in Scheme I.

Both the *endo*- and *exo*-DCP cations as well as the species responsible for the  $1.8\mu$  band produce the absorptions at 369 and 354 nm which are probable due to slightly perturbed cyclopentadiene cations (Figures 3–5 routes E, F, and I). Both the *endo*- and *exo*-DCP cations yield the  $1.7\mu$  band as Figures 4 and 5 and routes C and G show. In reference to the mechanisms proposed by Andrews et al.,<sup>15,16</sup> we tentatively assume a norcarene-like structure depicted in Scheme I under the frame  $1.7\mu$ band. Although this is purely speculative, the structureless broad absorption of the  $1.7\mu$  band does not seem to be incompatible with the assumed nonconjugative dienic structure. If the  $1.7\mu$  band is really associated with the norcarene-like cation, we can refer to the previous studies<sup>15,16</sup> to assume highly conjugated products shown in parenthesis for the 450–600-nm band in Scheme I. One of the products is considered to be the radical cation of decapentaene on the basis of the extrapolation of the observed spectra of the radical cations of hexatrienes,<sup>46,11b</sup> octatetraenes,<sup>11</sup> and the observation of analogous bands in solid argon directly from the matrix photoionization of decapentaene.<sup>11c</sup>

(3) 1,3-Bishomocubane. It is not surprising that the radical cation of 1,3-bishomocubane shows a structureless absorption in Figure 7. Radical cations of a number of saturated hydrocarbons show similar broad absorption bands.<sup>13</sup> The broad band in Figure 7 should comprise a number of different electronic excited states. Thus, the different photolytic results shown in the fine curve of Figure 7 and in Figure 8 are understandable: excitation with wavelengths near the red edge of the absorption in Figure 7 is associated with isomerization to the endo-DCP cation (route J with  $\lambda \gtrsim 1000$  nm) whereas shorter wavelengths of  $\lambda \gtrsim 690$  nm produce both the  $1.8\mu$  band and the 487-nm band by routes J and K. As mentioned in section 3.4, the 487-nm band is very photosensitive, and a rough estimation of the quantum yield of route L is 1 order of magnitude larger than that of route D. Definite characterization of the 487-nm band is not possible, but a provisional mechanism leading to the formation of a bicyclic cation is demonstrated in Scheme I for route K. Such a product may easily be ring-opened to give the products indicated in parentheses under the 450-600-nm band in Scheme I. Decisive assignments would be obtained if the assumed bicyclic hydrocarbon is prepared.

# 5. Conclusion

Major findings of the present work are summarized as follows: (1) The *endo*- and *exo*-DCP cations exhibit two distinctive absorption bands in the near-IR and near-UV regions (Figures 2(upper) and 5). The first broad bands are regarded as due to the intramolecular charge resonance in the bis-cyclopentaallylic radical cations.<sup>6</sup>

(2) The 1,3-bishomocubane cation exhibits a structureless absorption throughout the whole spectra region (Figure 7, broken curve). This is analogous to the result of a study on the radical cations of a number of saturated hydrocarbons.<sup>13</sup>

(3) Photoexcitation of the above three  $C_{10}H_{12}^{+,*}$ 's results in complicated changes summarized in Scheme I. The result of extensive photoexcitation is the production of a multitude of highly conjugated aliphatic hydrocarbons.

(4) The photoisomer obtained from the *endo*-DCP cation is identical with the product of a thermal dimerization between cyclopentadiene and its radical cation. The product exhibits a structured band in the near-IR and near-UV regions. By a process of elimination the product is inferred to be the radical cation of a new dicyclopentadiene which may have a rigid  $C_{2h}$  molecular structure.

Acknowledgment. The study was partially supported by the Subsidy for Scientific Research of the Ministry of Education in Japan, Grant No. 59430004.

**Registry No.** endo-DCP, 1755-01-7; exo-DCP, 933-60-8; cyclopentadiene, 542-92-7; 1,3-bishomocubane, 6707-86-4; trans-tricyclo-[3.0.3.0]deca-2,8-diene, 76024-07-2.

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<sup>(14)</sup> The authors are grateful to Professor Gerhard Closs and Dr. Thomas Bally for their suggestions of the bis-cyclopentaallylic structures for the radical cations of the *endo*- and the *exo*-DCP's.

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