109035-17-8; **47**, 109035-18-9; **47** (acetate), 109035-55-4; (*E*)-**48**, 109035-19-0; (*Z*)-**48**, 109035-56-5; (*E*)-**49**, 109035-20-3; (*Z*)-**49**, 109035-57-6; **52**, 109035-21-4; **53**, 109035-22-5; **54**, 109035-23-6; **55**, 84568-15-0; **56**, 109035-24-7; **57**, 84568-14-9; **58**, 109035-25-8; **59**, 109035-26-9; **60**, 109035-27-0; **61**, 109035-28-1; **62**, 109064-64-4; **63**, 109035-29-2; **64**, 109035-30-5; **71**, 88088-57-7; **72**, 109035-36-1; **73**, 109035-37-2; **74**, 109035-38-3; **75**, 109035-39-4; **76**, 109035-40-7; **77**, 109035-41-8; **77** (R^1 = H, R^2 = $CH_2C(Me)=CH_2$), 109035-33-8; **77** (R^1 = MOM, R^2 = $CH_2C(Me)=CH_2$), 109035-34-9; **77** (R^1 = MOM, R^2 = $CH_2CH(Me)CH_2OH$), 109035-35-0; **78**, 109035-42-9; **78** (R^1 = H, R^2 = $CH_2C(Me)=CH_2$), 109035-31-6; **78** (R^1 = MOM, R^2 = $CH_2C(Me)=CH_2$), 109035-32-7; $V(acac)_3$, 13476-99-8; $VO(acac)_2$, 3153-26-2; $Cr(acac)_3$, 21679-31-2; $Mn(acac)_2$, 14024-58-9; $Mn(acac)_3$, 14284-89-0; $Fe(acac)_3$, 14024-18-1; $Co(acac)_2$, 14024-48-7; $Co(acac)_3$, 21679-46-9; $Ni(acac)_2$, 3264-82-2; $Cu(acac)_2$, 13395-16-9; $Zn(acac)_2$, 14024-63-6; CuCl, 7758-89-6; CuBr, 7787-70-4; CuCN, 544-92-3; Cu_2O, 1317-39-1; CuOTf, 42152-44-3; Cu(acacen), 14263-53-7; $Cu(salad)_2$, 14523-25-2; Cu(salen), 14167-15-8; $Cu(dmg)_2$, 14221-10-4; $Cu(oxin)_2$, 10380-28-6; Cu(tpp), 14172-91-9; $Cu(F_3CCOCH=C(O^-)Me)_2$, 14324-82-4; $Cu(MeCOCH=C(O^-)Ph)_2$, 14128-84-8; $Cu(PhCOCH=C(O^-)Ph)_2$, 14405-48-2; $Cu(EtOCOCH=C(O^-)Me)_2$, 14284-06-1; $Cu(Me_3CCOCH=C(O^-)CMe_3)_2$, 14040-05-2; $Cu(MeCOC(Me)=C(O^-)Me)_2$, 14781-49-8; $Cl_2C=CCl_2$, 127-18-4; $ClCH_2OMe$, 107-30-2; $HOCH_2C(Me)=CH_2$, 513-42-8; $3\text{-}ClC_6H_4COCl$, 618-46-2; Cu, 7440-50-8; 2-bromo-3-(2,4-hexadienyl)naphthoquinone, 109035-46-3; 2-bromo-5-methoxy-6-methyl-3-(2,4-hexadienyl)-1,4-benzoquinone, 109035-47-4; *tert*-butyldimethylsilyl trifluoromethanesulfonate, 69739-34-0; allyltriphenylphosphonium bromide, 1560-54-9; ethyl crotonate, 10544-63-5; 4-bromo-3-(3,5-hexadienyl)-5-methoxy-6-methyl-1,2-benzoquinone, 109035-49-6; 4-bromo-3-(3,5-heptadienyl)-5-methoxy-6-methyl-1,2-benzoquinone, 109035-53-2; 3-bromo-2-(2,4-hexadienyl)-5-methyl-6-hydroxy-1,4-benzoquinone, 109035-50-9; 3-bromo-2-(2,4-heptadienyl)-5-methyl-6-hydroxy-1,4-benzoquinone, 109035-54-3; 4-bromo-3-(4-(ethoxycarbonyl)-3,5-hexadienyl)-5-methoxy-6-methyl-1,2-benzoquinone, 109035-58-7; 2-bromo-3-(4-(ethoxycarbonyl)-3,5-hexadienyl)-5-hydroxy-6-methyl-1,4-benzoquinone, 109035-59-8.

Silver(I)-Catalyzed Isomerization of Water-Soluble Quadricyclanes

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In aqueous ammonia, silver(I)-catalyzed isomerization of quadricyclanes to norbornadienes was investigated. The catalytic action of silver(I) perchlorate induced rapid and clean isomerization of water-soluble quadricyclanes **1b–g** to the corresponding norbornadienes **2b–g** even at room temperature. In the isomerization, the silver(I) catalyst might attack **1** from the five-membered ring, which was different from the directions observed in the cobalt(II)–porphyrin- and rhodium(I)-catalyzed reactions. The present reactions proceed via the formation of the cationic species and the successive cleavage of the highly strained cyclopropane ring of **1** to give **2**.

It is well-known that silver(I) salts are useful for organic synthesis, and especially effective for the ring cleavage of organic molecules.[1] The mechanisms of silver(I)-catalyzed reactions have been discussed, and most of them indicate that the cationic species induced by silver(I) may be the reaction intermediates.[1] Typically, silver(I) accelerated the isomerization of quadricyclanes to norbornadienes,[2] and a cationic species was widely recognized as the intermediate.[3]

In the above reactions, the attacking direction of silver(I) is important but has not been investigated. Recently, it was shown that silver(I) might attack from one of the exo directions of quadricyclanes in bezene.[4] Here, we report first that silver(I) salts are effective for the isomerization of some water-soluble quadricyclanes **1b–g** to norbornadienes **2b–g** in aqueous ammonia and then discuss the reaction pathway.

Results and Discussion

Water-soluble cobalt–porphyrin complexes were effective catalysts for the isomerization of water-soluble quadricyclanes to the corresponding norbornadienes in an aqueous sodium carbonate solution (see ref 5). In this system, however, introduction of a methyl group at the R position in quadricyclanes **1** (see Table I) reduced remarkably the rate of the isomerization induced by cobalt tetrakis(*p*-carboxyphenyl)porphyrin (Co-TPPC). To overcome this disadvantage, we examined several catalysts and found that silver salts were effective for the isomerization. For example, when silver perchlorate (0.1 mg) was added to an aqueous ammonia solution (0.5 mL) of quadricyclane **1b** at room temperature, **1b** isomerized to norbornadiene **2b** suddenly and cleanly, and the half-life of **1b** was about 7 min at 25 °C (see Table I). On the other hand, addition of silver perchlorate to nonsubstituted **1a** in aqueous ammonia induced the formation of undesirable byproducts, water adducts **3a** and other unknowns, in addition to the slow isomerization to **2a**.

Acceleration of the isomerization rate by substitution of a methyl group at the R position could support the theory that the reaction intermediate in aqueous ammonia was the cationic species charged partially on the adjacent carbon of the R position. Taking into consideration the fact that water adducts could not be observed during the isomerization of **1b** to **2b**, water might not have trapped

(1) Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461.

(2) (a) Isomerization of quadricyclanes to norbornadienes has been of interest to many chemists as one of the solar energy storage systems. Therefore, a lot of catalysts, including silver(I), have been investigated. See: Maruyama, K.; Tamiaki, H.; Kawabata, S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 543 and references therein. (b) Recent reports after the above paper are as follows. Cobalt–porphyrin catalysts: Wöhrle, D.; Buttner, P. *Polym. Bull. (Berlin)* **1985**, *13*, 57. Datta, R.; Rydant, J.; Rinker, R. G. *J. Catal.* **1985**, *95*, 202. Smierciak, R. C.; Giordano, P. J. *Appl. Catal.* **1985**, *18*, 353. Maruyama, T.; Yoshida, Z.; Miki, S. *J. Chem. Eng. Jpn.* **1985**, *18*, 515. Miki, S.; Ohno, T.; Iwasaki, H.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 3487. Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1986**, *819*. Yamashita, Y.; Hanaoka, T.; Takeda, Y.; Mukai, T. *Ibid.* **1986**, 1279. Kamogawa, H.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1501. Palladium catalysts: Yoshida, Z. *J. Photochem.* **1985**, *29*, 27. Khusnutdinov, R. I.; Dokichev, V. A.; Popova, I. O.; Nefedov, O. M.; Tolstikov, G. A.; Dzhemilev, U. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1985**, *34*, 433. Photon: Kelley, C. K.; Kutal, C. *Organometallics* **1985**, *4*, 1351. Kajitani, M.; Kohara, M.; Kitayama, T.; Asano, Y.; Sugimori, A. *Chem. Lett.* **1986**, 2109. Draper, A. M.; de Mayo, P. *Tetrahedron Lett.* **1986**, *27*, 6157.

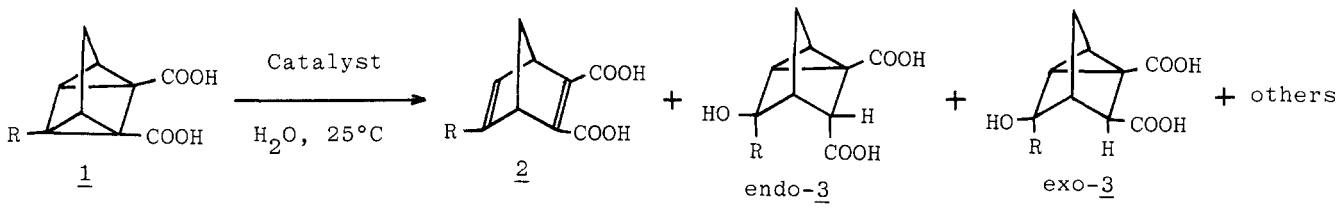
(3) (a) Nelsen, S. F.; Gillespie, J. P.; Hintz, P. J. *Tetrahedron Lett.* **1971**, *12*, 2361. (b) Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1987**, 485.

(4) Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1987**, 683.

(5) Maruyama, K.; Tamiaki, H. *J. Org. Chem.* **1986**, *51*, 602.

0022-3263/87/1952-3967$01.50/0

Table I. Catalytic Reaction of Quadricyclanes in an Aqueous Alkaline Solution

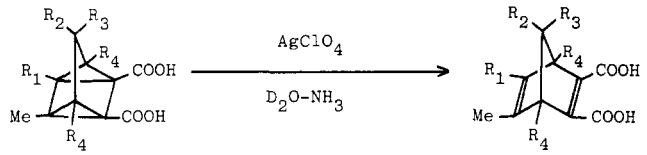


1 2 endo-3 exo-3

R	no.	alkali	catalyst (concn, mM)	time, min	yield,[a] % 2	*endo*-3	*exo*-3	others	1
H	1a	Na_2CO_3	Co-TPPC (1)	1	~50	0	0	0	~50
				10	100	0	0	0	0
Me	1b	Na_2CO_3	Co-TPPC (1)	10	4	0	0	0	96
				100	34	0	0	0	66
H	1a	NH_3	$AgClO_4$ (1)	60	0	0	0	0	100
			$AgClO_4$ (10)	6000	9	4	5	8	74
Me	1b	NH_3	$AgClO_4$ (1)	10	62	0	0	0	38
				60	100	0	0	0	0

[a] All yields were determined by means of ^1H NMR.

Table II. Isomerization Rate Constant *k* of Quadricyclanes



1b-g 2b-g

	R_1	R_2	R_3	R_4	k,[a] M^{-1} s^{-1}
b	H	H	H	H	1.6
c	Me	H	H	H	0.57
d	H	Me	Me	H	0.11
e	Me	Me	Me	H	0.10
f	Me	Me	H	Me	~50
g	Me	H	Me	Me	5.3

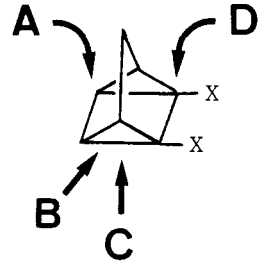
[a] k was determined by means of ^1H NMR ([1] = 0.02 M, in 0.1 M NH_3-D_2O, at 25 °C). Error was within ±8%.

such a cationic species.[6] Sodium perchlorate had no catalytic activity, but both siver nitrate and silver sulfate had the same activity as silver perchlorate. The above facts led to the conclusion that silver(I) (or diamminesilver(I)) produced the cationic species as the reaction intermediate.

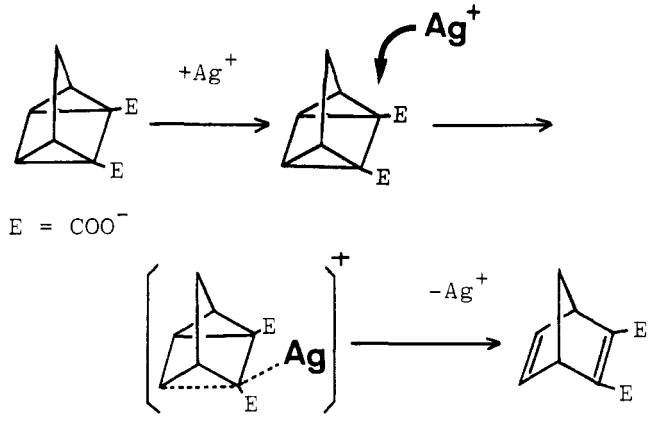
To clarify the structure of the intermediate and the route to the intermediate, isomerization of several quadricyclanes **1b–g** was investigated (see Table II). By addition of a catalytic amount of silver perchlorate, all **1b–g** in aqueous ammonia isomerized to norbornadienes **2b–g** immediately and quantitatively. The initial isomerization rate obeyed pseudo-first-order kinetics, and the apparent second-order rate constants k were determined by ^1H NMR technique (see the Experimental Section).

The apparent second-order rate constant k in the initial stage of the isomerization of **1b** to **2b** was 1.6 M^{-1} s^{-1} and that of **1c**, methylated at the R_1 position of **1b**, was 0.57 M^{-1} s^{-1}, which was slightly smaller than that of **1b**. Substitution with two methyl groups at the R_2 and R_3 positions of **1b**, as in **1d**, suppressed k considerably ($k_{1d\rightarrow 2d}/k_{1b\rightarrow 2b}$ ~ 1/15). Similarly, methylation at both the positions of **1c**, as in **1e**, reduced k. Moreover, the k values of **1d** and of **1e**, methylated at the R_1 position of **1d**, were nearly equal. In contrast, the rate k of **1f**, substituted with methyl

Chart I. Attacking Direction



Scheme I. Reaction Pathway in Silver(I)-Catalyzed Isomerization



groups at the R_1, R_2, and R_4 positions of **1b** (R_3 = H), was about 50 M^{-1} s^{-1} and nearly 10 times larger than that of **1g**, methylated at the R_1, R_3, and R_4 positions (R_3 = Me). The above results show that the introduction of a methyl group at the R_3 position decreases k. Therefore, it is supposed that the silver(I) catalyst might attack **1** from the D direction (see Chart I).

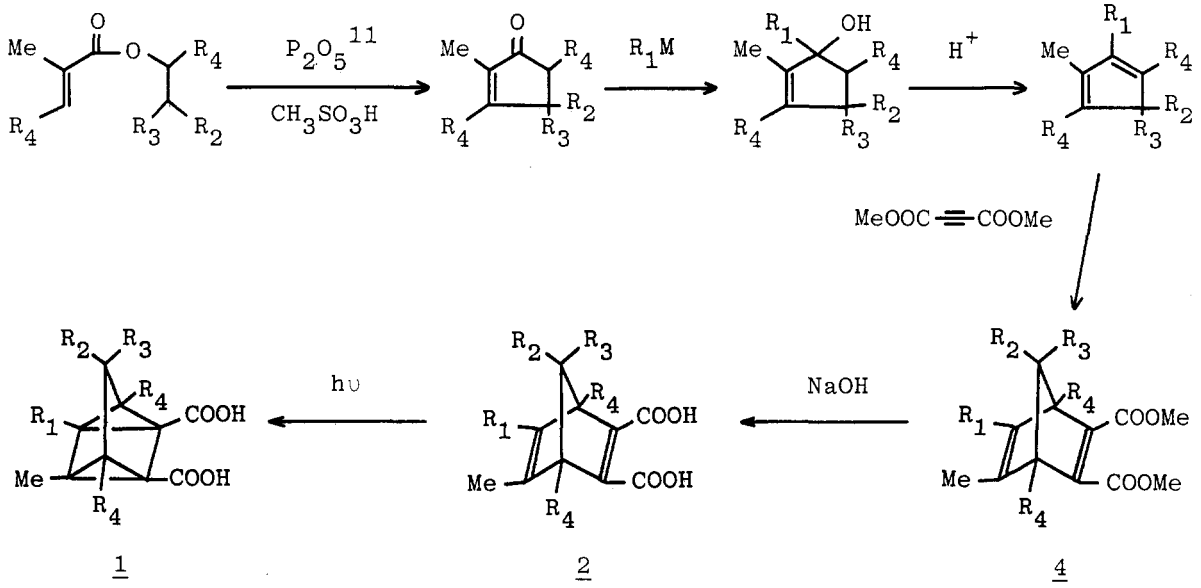
The D direction is different from the A direction suggested in the cobalt(II)–porphyrin-catalyzed isomerization of **1** to **2**[5] and from the B or C direction in the nickel(0)[7]- and rhodium(I)[8]-catalyzed isomerization of quadricyclane

(6) In methanol, similar results were obtained; see ref 3b. In the investigation, it was found that a proton catalyzed the addition of methanol to quadricyclanes. Therefore, a proton might induce the formation of **3**.

(7) (a) Noyori, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *J. Am. Chem. Soc.* **1975**, *97*, 812. (b) In the siliver(I)-catalyzed isomerization of dicarbomethoxybishomocubane, the similar attacking direction was proposed on the basis of the extended Hückel MO calculation. Noyori, R.; Yamakawa, M.; Takaya, H. *J. Am. Chem. Soc.* **1976**, *98*, 1471. Noyori, R. *Adv. Chem. Ser.* **1979**, *No. 173*, 307.

(8) Cassar, L.; Halpern, J. *J. Chem. Soc. D.* **1970**, 1082.

Scheme II. Synthetic Route to Quadricyclanes



to norbornadiene. The attacking direction in the silver(I)-catalyzed isomerization may be ascribed to the Lewis acid nature of silver(I): a relatively good σ-acceptor and a poor π-donor.[1,7b] Consequently, in the isomerization of **1** to **2** in aqueous ammonia,[9] the reaction pathway might be shown as given in Scheme I.[10]

Concluding Remarks

It was first observed that silver(I) salts were effective for the isomerization of quadricyclanes to norbornadienes in aqueous ammonia. The catalytic reaction in aqueous ammonia proceeds via a cationic intermediate; the mechanism is similar to that in benzene, an aprotic solvent. The cleanliness of the catalytic reaction and the similarity of the mechanisms are surprising, taking account of the fact that a silver(I) catalyst, a Lewis acid and water solvent, a Lewis base coexist in the reaction solution. The attacking direction of silver(I) catalysts is just the reverse to that of cobalt–porphyrin catalysts toward methylated quadricyclanes that isomerize rapidly to norbornadienes.

Experimental Section

Apparatus. All melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a JEOL JNM-FX400 instrument; chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Mass specta were measured with a JEOL JMS-DX-300 spectrometer.

Materials. The compounds **1a–c** and **2a–c** were synthesized according to the procedures given in the literature,[5] and other compounds, **1d–g** and **2d–g**, were prepared as shown in Scheme II.

Dimethyl 5,7,7-Trimethyl-2,5-norbornadiene-2,3-dicarboxylate (4d). In the usual way, the reaction of 2,4,4-trimethyl-2-cyclopentenone[12] (620 mg, 5.0 mmol) and lithium aluminum hydride in dry ether gave 2,4,4-trimethyl-2-cyclopentenol. To a benzene solution (30 mL) of the alcohol were added a piece of *p*-toluenesulfonic acid and dimethyl acetylenedicarboxylate (500 μL, 4.1 mmol). The solution was refluxed for 12 h under nitrogen in the dark. The solution was cooled, washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and then distilled. The ester **4d** was obtained in a yield of 94% (953 mg). *Caution*! Norbornadienes **2b–g** and **4b–g** were fairly photosensitive, isomerizing to the corresponding quadricyclanes upon irradiation even with household electric lights in the laboratory, and had to be handled and stored in the dark: pale yellow oil; bp 104 °C (0.5 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.14 (3 H, s), 1.17 (3 H, s), 1.90 (3 H, d, J = 2 Hz), 3.15 (1 H, dd, J = 1, 3 Hz), 3.37 (1 H, t, J = 3 Hz), 3.765 (3 H, s), 3.768 (3 H, s), 6.15–6.17 (1 H, m); IR (neat) 1710 (C=O), 1635, 1615 cm^{-1} (C=C); MS, calcd for $C_{14}H_{18}O_4$ m/e 250.1205, found m/e 250.1198 (M^+).

5,7,7-Trimethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2d). The base-catalyzed hydrolysis[5] of the ester **4d** gave the acid **2d** in a yield of 100%: pale yellow needles; mp 117–120 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.13 (3 H, s), 1.18 (3 H, s), 1.91 (3 H, d, J = 2 Hz), 3.49 (1 H, dd, J = 1, 3 Hz), 3.68 (1 H, t, J = 3 Hz), 6.17–6.20 (1 H, m); IR (KBr) 1680, 1625 (C=O), 1555 cm^{-1} (C=C); MS, calcd for $C_{12}H_{14}O_4$ m/e 222.0892, found m/e 222.0890 (M^+).

5,7,7-Trimethylquadricyclane-2,3-dicarboxylic Acid (1d). At 0 °C a dry ether solution of norbornadiene **2d** in a Pyrex tube under argon was irradiated with a 300-W high-pressure mercury arc lamp through a filter of aqueous saturated copper sulfate solution for 1 h. The solvent was evaporated at 0 °C to give reasonably pure quadricyclane **1d** quantitatively. *Caution*! In neutral organic solvents, quadricyclanes **1b–g** were thermally unstable, isomerizing to **2b–g** at room temperature, and had to be handled and stored below 0 °C: white crystals; ^{1}H NMR ($CDCl_3$) δ 1.22 (3 H, s), 1.27 (3 H, s), 1.53 (3 H, s), 2.10 (1 H, d, J = 2 Hz), 2.28 (1 H, dd, J = 2, 5 Hz), 2.67 (1 H, d, J = 5 Hz); IR (KBr) 1685, 1620 cm^{-1} (C=O).

Dimethyl 5,6,7,7-Tetramethyl-2,5-norbornadiene-2,3-dicarboxylate (4e). In the same manner as the synthesis of **4d** except using methylmagnesium iodide instead of lithium aluminum hydride, the ester **4e**[13] was obtained in a yield of 79%: yellow oil; bp 94 °C (0.35 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.10 (3 H, s), 1.12 (3 H, s), 1.74 (6 H, s), 3.12 (2 H, s), 3.77 (6 H, s); IR (neat) 1710 (C=O), 1620 cm^{-1} (C=C); MS, calcd for m/e $C_{15}H_{20}O_4$ 264.1361, found m/e 236.1347 (M^+).

5,6,7,7-Tetramethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2e). The base-catalyzed hydrolysis[5] of **4e** gave **2e** in a yield of 95%: yellow needles; mp 160–162 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.08 (3 H, s), 1.14 (3 H, s), 1.76

(9) In 0.1 M NH_4OH, the solution was about pH 11 and both **1** and **2** might release two protons to afford the dianions of **1** and **2**. See: Carroll, F. A.; Green, D. K.; Sloop, J. C. *Sol. Energy* **1984**, *33*, 377.

(10) Another possibility that could not be ruled out was that silver(I) attacked the carbonyl oxygen after the approach from the D direction. See ref 3a and: Cristol, S. J.; Harrington, J. K.; Morrill, T. C.; Greenwald, B. E. *J. Org. Chem.* **1971**, *36*, 2773.

(11) Conia, J.-M.; Leriverend, M.-L. *Bull. Soc. Chim. Fr.* **1970**, *2981*. Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.

(12) Gowda, G.; McMurry, T. B. H. *J. Chem. Soc. Perkin Trans. 1* **1979**, 274.

(13) Ester **4e** was already prepared: Hirao, K.; Ando, A.; Hamada, T.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 300.

(6 H, s), 3.45 (2 H, s); IR (KBr) 1690, 1610 (C=O), 1555 cm^{-1} (C=C); MS, calcd for $C_{13}H_{16}O_4$ *m/e* 236.1048, found *m/e* 236.1007 (M^+).

5,6,7,7-Tetramethylquadricyclane-2,3-dicarboxylic Acid (1e). In the same manner as the synthesis of **1d**, the photolysis of **2e** in ether gave **1e** quantitatively. Another method could be also adapted in the preparation of **1e**. When the solid of **2e** in a Pyrex tube was irradiated with sunlight, usual fluorescent light in laboratory, or a high-pressure mercury arc lamp (with or without a filter of aqueous $CuSO_4$), the yellow needles turned white. The white needles were pure **1e** containing no byproduct: mp 154–156 °C; ^1H NMR ($CDCl_3$) δ 1.20 (3 H, s), 1.22 (3 H, s), 1.49 (6 H s), 2.13 (2 H, s); IR (KBr) 1680, 1615 cm^{-1} (C=O); MS, calcd for $C_{13}H_{16}O_4$ *m/e* 236.1048, found *m/e* 236.1049 (M^+).

Dimethyl 1,4,5,6,*anti*-7-Pentamethyl-2,5-norbornadiene-2,3-dicarboxylate (4f) and Dimethyl 1,4,5,6,*syn*-7-Pentamethyl-1,2,5-norbornadiene-2,3-dicarboxylate (4g). To a dry ether solution (10 mL) of methylmagnesium iodide (2.5 mmol) was dropwise added 2,3,4,5-tetramethyl-2-cyclopentenone[14] (276 mg, 2.0 mmol) with stirring at 0 °C under nitrogen. After addition, the solution was refluxed for 1 h, quenched with saturated aqueous NH_4Cl, and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and then concentrated to give 1,2,3,4,5-pentamethylcyclopentadiene. To a benzene solution (30 mL) of the diene was added dimethyl acetylenedicarboxylate (184 μL, 1.5 mmol) at room temperature under nitrogen. The solution was stirred for 1 h and distilled. A mixture of the two isomers (**4f**/**4g** = 62/38) was obtained at 108 °C (0.7 mmHg) in a yield of 94% (392 mg, 1.4 mmol). Two recrystallizations from hexane gave pure **4f**. The first mother liquid was concentrated and the residue was redistilled to give pure **4g**. **4f**: white plates; mp 94–95 °C; ^1H NMR ($CDCl_3$) δ 0.70 (3 H, d, J = 6 Hz), 1.25 (6 H, s), 1.63 (6 H, s), 2.34 (1 H, q, J = 6 Hz), 3.73 (6 H, s); IR (KBr) 1710 (C=O), 1600 cm^{-1} (C=C); MS, calcd for $C_{16}H_{22}O_4$ *m/e* 278.1518, found *m/e* 278.1501 (M^+). **4g**: white crystals; bp 85 °C (0.1 mmHg); mp 53–55 °C; ^1H NMR ($CDCl_3$) δ 0.84 (3 H, d, J = 6 Hz), 1.25 (6 H, s), 1.68 (6 H, s), 2.12 (1 H, q, J = 6 Hz), 3.72 (6 H, s); IR (KBr) 1725, 1705 (C=O), 1605 cm^{-1} (C=C); MS, calcd for $C_{16}H_{22}O_4$ *m/e* 278.1518, found *m/e* 278.1540 (M^+).

1,4,5,6,*anti*-7-Pentamethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2f). The base-catalyzed hydrolysis[5] of **4f** gave **2f** in a yield of 97%: white crystals; mp 182–185 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 0.75 (3 H, d, J = 6 Hz), 1.34 (6 H, s), 1.65 (6 H, s), 2.28 (1 H, q, J = 6 Hz); IR (KBr) 1695 (C=O), 1610 cm^{-1}; MS, calcd for $C_{14}H_{18}O_4$ *m/e* 250.1205, found *m/e* 250.1202 (M^+).

1,4,5,6,*anti*-7-Pentamethylquadricyclane-2,3-dicarboxylic Acid (1f). In the same manner as the synthesis of **1d**, the photolysis of **2f** in ether gave **1f** quantitatively: white cyrstals; ^1H NMR ($CDCl_3$) δ 1.01 (3 H, d, J = 7 Hz), 1.32 (6 H, s), 1.34 (6 H, s), 2.40 (1 H, q, J = 7 Hz); IR (KBr) 1680, 1595 cm^{-1} (C=O); MS, *m/e* 250 (M^+).

1,4,5,6,*syn*-7-Pentamethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2g). The base-catalyzed hydrolysis[5] of **4g** gave **2g** in a yield of 97%: white crystals; mp 199–201 °C (from dichloromethane and hexane); ^1H NMR ($CDCl_3$) δ 0.84 (3 H, d, J = 6 Hz), 1.32 (6 H, s), 1.69 (6 H, s), 2.16 (1 H, q, J = 6 Hz); IR (KBr) 1710, 1670 (C=O), 1615 cm^{-1}; MS, calcd for $C_{14}H_{18}O_4$ *m/e* 250.1205, found *m/e* 250.1187 (M^+).

1,4,5,6,*syn*-7-Pentamethylquadricyclane-2,3-dicarboxylic Acid (1g). In the same manner as the synthesis of **1d**, the photolysis of **2g** in ether gave **1g** quantitatively: white crystals; ^1H NMR ($CDCl_3$) δ 1.08 (3 H, d, J = 6 Hz), 1.30 (6 H, s), 1.37 (6 H, s), 2.25 (1 H, q, J = 6 Hz); IR (KBr) 1670, 1605 cm^{-1} (C=O); MS, *m/e* 250 (M^+).

Preparation of Water Adducts 3a. Quadricyclane **1a** in water was refluxed for 1 h, and the solvent was evaporated to give two isomers of water adducts **3a** (endo/exo = 53/47). *endo*-**3a**: ^1H NMR (D_2O) δ 1.50 (1 H, d, J = 12 Hz), 1.81 (1 H, d, J = 12 Hz), 1.99 (1 H, d, J = 5 Hz), 2.03 (1 H, d, J = 5 Hz), 2.08 (1 H, s), 2.71 (1 H, d, J = 2 Hz, C*H*COOH), 4.00 (1 H, t, J = 2 Hz, C*H*OH). *exo*-**3a**: ^1H NMR (D_2O) δ 1.52 (1 H, d, J = 12 Hz), 1.68 (1 H, d, J = 12 Hz), 1.90 (1 H, d, J = 5 Hz), 2.06 (1 H, d, J = 5 Hz), 2.10 (1 H, s), 2.64 (1 H, d, J = 2 Hz, C*H*COOH), 3.86 (1 H, t, J = 2 Hz, C*H*OH).

The reaction of these diacids, **3a**, and diazomethane afforded two isomers of dimethyl esters. These isomers were separated by using flash column chromatography over silica gel with dichloromethane and methanol as eluants. Dimethyl ester of *endo*-**3a**:[15] ^1H NMR ($CDCl_3$) δ 1.60 (1 H, br d, J = 3 Hz), 1.61 (1 H, dt, J = 11, 1 Hz), 2.05 (1 H, dd, J = 1, 5 Hz), 2.13 (1 H, d, J = 11 Hz), 2.21 (1 H, s), 2.22 (1 H, dt, J = 5, 1 Hz), 2.83 (1 H, d, J = 1 Hz, C*H*COOMe), 3.66 (3 H, s), 3.70 (3 H, s), 4.34 (1 H, s, C*H*OH). Dimethyl ester of *exo*-**3a**:[15] ^1H NMR ($CDCl_3$) δ 1.67 (1 H, br d, J = 3 Hz), 1.81 (1 H, dt, J = 11, 1 Hz), 1.92 (1 H, d, J = 11 Hz), 1.97 (1 H, dt, J = 5, 1 Hz), 2.22 (1 H, s), 2.25 (1 H, dd, J = 1, 5 Hz), 2.75 (1 H, d, J = 2 Hz, C*H*COOMe), 3.66 (3 H, s), 3.69 (3 H, s), 4.03 (1 H, s, C*H*OH).

Measurement of Initial Second-Order Rate Constants. An NH_3–D_2O solution of **1** was added to an NH_3–D_2O solution of silver perchlorate in a NMR sample tube at 25 °C ([**1**] = 0.02 M, in 0.1 M NH_3–D_2O, pH ~11). ^1H NMR signals of **1** and **2** were integrated at an appropriate time interval. Molar quantities of **1** and **2** were calculated, and $-\ln [[1]/([1] + [2])]$ was plotted vs. time, which gave a straight line in the initial stage of the reaction. Until at least 1 half-life, the rate obeyed pseudo-first-order kinetics within experimental error. The initial second-order rate constant was determined[2a] and was an average value of three measurements, at least. In basic solvents, typically in an aqueous ammonia solution, quadricyclanes **1b–g** were thermally stable, isomerizing to **2b–g** very slowly at room temperature. Under the above conditions, the thermal isomerization ($<1 \times 10^{-5}$ s^{-1}) was negligible during the measurement.

Registry No. **1b**, 100165-63-7; **1c**, 100165-64-8; **1d**, 109467-30-3; **1e**, 109467-31-4; **1f**, 109467-32-5; **1g**, 109581-99-9; **2d**, 109467-34-7; **2e**, 109467-35-8; **2f**, 109494-83-9; **2g**, 109494-84-0; *endo*-**3a**, 109467-38-1; *exo*-**3a**, 109582-00-5; *endo*-**3a** dimethyl ester, 109467-39-2; *exo*-**3a** dimethyl ester, 109582-01-6; **4d**, 109494-73-7; **4e**, 90407-72-0; **4f**, 109467-36-9; **4g**, 109467-37-0; Co-TPPC, 19414-69-8; $AgClO_4$, 7783-93-9; 2,4,4-trimethyl-2-cyclopentenone, 17190-21-5; 2,4,4-trimethyl-2-cyclopentenol, 109467-33-6; dimethyl acetylenedicarboxylate, 762-42-5; 2,3,4,5-tetramethyl-2-cyclopentenone, 54458-61-6; 1,2,3,4,5-pentamethylcyclopentadiene, 4045-44-7.

(14) Feitler, D.; Whitesides, G. M. Inorg. *Chem.* **1976**, *15*, 466.

(15) Dimethyl esters of **3a** were already prepared: Behr, A.; Keim, W.; Thelen, G.; Scharf, H.-D.; Ressler, I. *J. Chem. Technol. Biotechnol.* **1982**, *32*, 627.