Catalytic Isomerization of Water-Soluble Quadricyclane to Norbornadiene Derivatives Induced by Cobalt-Porphyrin Complexes

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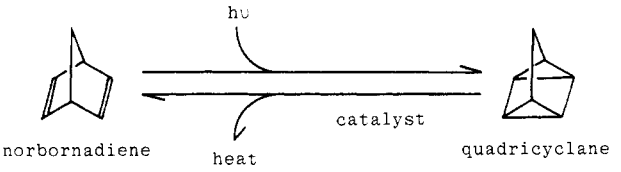
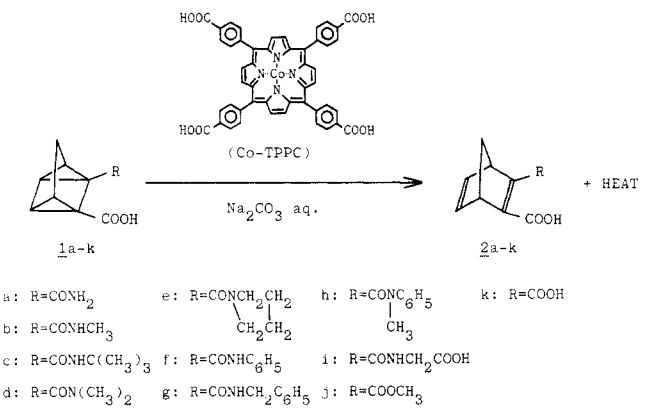
In an aqueous alkaline solution, the exothermic isomerization of quadricyclane derivatives to norbornadiene derivatives catalyzed by cobalt-porphyrin complexes was investigated. By catalytic action of cobalt 5,10,15,20-tetrakis(*p*-carboxyphenyl)porphyrin (Co-TPPC),[1] thermally stable and water-soluble quadricyclane derivatives **1a-l** isomerized to the corresponding norbornadiene derivatives **2a-l** quantitatively and suddenly even at room temperature in an aqueous sodium carbonate solution. It was seen that larger hydrophobicities of **1** enhanced the isomerization rate. The attacking direction of cobalt porphyrins toward quadricyclanes might be to the five-membered ring, which was different from that suggested in the action of Rh catalyst, i.e., attack to the three-membered ring.

Rearrangement of a small organic molecule catalyzed by a transition metal has attracted much attention from the viewpoints of organic syntheses and reaction mechanisms.[2] Especially, isomerization of quadricyclane to norbornadiene has been extensively investigated to establish an efficient solar energy storage system.[3] However, scant information on the reaction mechanism is available at the present. All of the reactions investigated so far used an organic solvent as the reaction medium. For practical use, we first succeeded in using water as the reaction medium.[4] In the present work, we have investigated the catalytic isomerization of a large number of water-soluble quadricyclane derivatives **1** to the corresponding norbornadiene derivatives **2** by a water-soluble cobalt-porphyrin complex in aqueous alkaline solution in order to elucidate the reaction mechanism (Scheme I).

Scheme I. Valence Isomerization



Scheme II. Heat-Releasing Process



Results and Discussion

Water-soluble quadricyclane derivatives **1a-k** were thermally stable in an aqueous sodium carbonate solution and neither isomerized to the corresponding norbornadiene derivatives **2a-k** nor reacted with water at room temperature.[5] However, addition of Co-TPPC to an aqueous sodium carbonate solution of **1** induced quantitative isomerization to **2** with the release of heat (Scheme II). As a typical example, when Co-TPPC (1 mg) was added to an aqueous sodium carbonate solution (1 ml) of **1b** at 25 °C, the half-life of **1b** was about 3.5 min, and the heat of the isomerization was about 52 kJ mol^{-1}.[3a] The isomerization rate obeyed pseudo-first-order kinetics, and the rate constants k are tabulated in Table I.

The rate constant k of nonsubstituted amide **1a** and those of *N*-monoalkyl amides **1b,c** were nearly the same but were smaller than those of *N,N*-dialkyl amides **1d,e**. In N-monosubstituted amides, the k values of **1f,g** having a phenyl group in the molecule were larger than those of **1b,c**. Moreover, the k value of N,N-disubstituted amide **1h** with a phenyl substituent was about 10-times larger than those of **1a-g**. The compound **1i** having the second

Table I. Second-Order Rate Constant k^a of Quadricyclane Derivatives

	R	$k/M^{-1}\ s^{-1}$ Co-TPPC/ D_2O-Na_2CO_3	$k/M^{-1}\ s^{-1}$ Co-TPP/ $CDCl_3$
a	$CONH_2$	2.6	
b	$CONHCH_3$	2.8[b]	7.6[b]
c	$CONHC(CH_3)_3$	2.5	
d	$CON(CH_3)_2$	3.9	4.5
e	$CONCH_2CH_2CH_2CH_2$	6.9	
f	$CONHC_6H_5$	6.7[b]	6.4[b,c]
g	$CONHCH_2C_6H_5$	5.6	
h	$CON(CH_3)C_6H_5$	61.6	3.7
i	$CONHCH_2COOH$	2.0	
j	$COOCH_3$	22.3	7.5
k	COOH	9.6	

[a] Error was within ±8% (at 25 °C). [b] See ref 3. [c] In CD_3COCD_3.

(1) The following abbreviations are used in this paper; TPPC = 5,10,15,20-tetrakis(*p*-carboxyphenyl)porphyrin dianion, TPP = 5,10,15,20-tetraphenylporphyrin dianion, TPP(*o*-Me) = 5,10,15,20-tetrakis(*o*-tolyl)porphyrin dianion, TPP(*p*-Me) = 5,10,15,20-tetrakis(*p*-tolyl)porphyrin dianion, TMP = 5,10,15,20-tetrakis(2,4,6-mesityl)porphyrin dianion.

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

(3) (a) Maruyama, K.; Tamiaki, H.; Kawabata, S. *J. Chem. Soc., Perkin Trans. 2*, in press and references cited therein. (b) Catalytic activities of cobalt porphyrins were already reported: Manassen, J. *J. Catal.* **1970**, *18*, 38. Wilson, H. D.; Rinker, R. G. *Ibid.* **1976**, *42*, 268. King, R. B.; Sweet, E. M. *J. Org. Chem.* **1979**, *44*, 385. Hautala, R. R.; King, R. B.; Kutal, C. "Solar Energy; Chemical Conversion and Storage", Humana Press: Clifton, NJ, 1979; pp 333-369.

(4) Maruyama, K.; Tamiaki, H. *Chem. Lett.* **1982**, 1699.

(5) (a) Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950. (b) Berr, A.; Keim, W.; Thelen, G.; Scharf, H.-D.; Ressler, I. *J. Chem. Tech. Biotechnol.* **1982**, *32*, 627. (c) Carroll, F. A.; Green, D. K.; Sloop, J. C. *Sol. Energy* **1984**, *33*, 377.

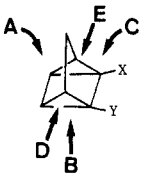
0022-3263/86/1951-0602$01.50/0

Table II. Isomerization Rate Constant k.[a] Dependence upon Initial Concentration of 1b

[1b]/M	k/M^{-1} s^{-1}
0.049	2.6
0.104	2.8
0.196	2.6
0.515	2.5

[a] Error was within ±15% ([Co-TPPC] = 7 × 10^{-4} M, at 25 °C).

Scheme III. Attacking Direction

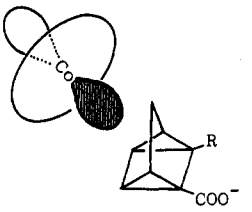


carboxyl group in the molecule showed smaller k than **1b**. The same behavior was also observed in the isomerization of monoacid–monoester **1j** and diacid **1k**. Therefore, removal of the amido hydrogen and the second carboxyl group from a water-soluble quadricyclane derivative and introduction of a phenyl group increased its isomerization reactivity in an aqueous alkaline solution.

Considering that the rate constant k was independent of the initial concentration of **1b** (Table II), we could suppose that the decrease of k by introducing the amido hydrogen and the carboxyl group in the molecule might not be ascribed to their coordination to the active site of the catalyst.[6] From the facts described above, it is clear that more hydrophobic quadricyclane derivatives **1a–i** show larger k in an aqueous solution. In a chloroform solution, different behavior from that in an aqueous solution was observed (Table I). The active site of the catalyst Co–TPPC may be at the axial sites[3a] and the site may behave hydrophobically because of the peripheral tetraphenylporphyrin skeleton.[7] Therefore, approach of water-soluble quadricyclane derivatives **1** toward the hydrophobic field around the active site of Co–TPPC is associated with the rate-determining step, which is a key step of the isomerization of **1a–k** to **2a–k** in an aqueous alkaline solution.

After approaching, which site of a quadricyclane derivative was most reactive toward the axial site of Co–TPPC? To investigate the situation, we measured the isomerization rate constants k of the methyl-substituted quadricyclane derivatives **1l–q** (see Table III). The rate constant k of nonsubstituted diacid **1k** was about 1 × 10 M^{-1} s^{-1}, and that of **1l**, methylated at the R_1 position of **1k**, was 4 × 10 M^{-1} s^{-1}, which was 4 times larger than that of **1k**.[8]

Scheme IV. A Possible Intermediate



Substitution with a methyl group at the R_2 position of **1k**, as in **1m**, suppressed k substantially ($k_{1m\rightarrow 2m}/k_{1k\rightarrow 2k} \sim 1/140$). The rate constant k of **1n**, substituted by two methyl groups at the R_2 and R_3 positions of **1k**, was less than 5 × 10^{-3} M^{-1} s^{-1} and smaller than that of **1m**. On the other hand, substitution with a methyl group at the R_4 position, as in **1o**, changed k only a little, but that at the R_5 position, as in **1p**, reduced k markedly ($k_{1p\rightarrow 2p}/k_{1o\rightarrow 2o} \sim 1/20000$). Moreover, substitution with methyl groups at the R_4 and R_5 positions, as in **1q**, affected k much more dramatically; k of **1q** was decreased to 9 × 10^{-4} M^{-1} s^{-1}, which was about 10^{-4} times smaller than that of **1k**. As noted above, introduction of several groups to one side (X and Y positions, see Scheme III) of a quadricyclane molecule as in **1a–k** affected the isomerization rate constants k only slightly; i.e., the difference was at most a factor of 30. In contrast, substitution with methyl groups at the opposite side as in **1m,n,p,q** affected k greatly by over 3 orders of magnitude. With increasing the steric hindrance toward attack from the A direction (see Scheme IV), k decreased drastically. Therefore, we suggest that an axial site of Co–TPPC may attack **1** from the A direction.

This direction is different from those (B, D, or E) suggested by J. Halpern et al.[9] in the isomerization of quadricyclane to norbornadiene catalyzed by Rh complexes in an organic solvent. We therefore examined the isomerization of several quadricyclane derivatives catalyzed by cobalt–porphyrin complexes in an organic solvent. As is clear from Table IV, a similar tendency[10] as in an aqueous sodium carbonate solution was observed in the isomerization of **3a–f** to **4a–f** catalyzed by Co–TPP in a benzene solution.[11]

Moreover, in the case of **3c**, the reactivities of cobalt porphyrins were suppressed by increasing bulkiness around their axial sites in the following order: Co–TPP ~ Co–TPP(*p*-Me) > Co–TPP(*o*-Me) > Co–TMP.[12] From a comparison of the isomerization by Co–TPP with that by Co–TMP, neither **3a** nor **3d** showed decrease of the isomerization rate, but **3b** showed a smaller decrease than **3c**. Both **3e** and **3f** showed a little greater rate decrease compared with **3c** by changing catalyst from Co–TPP to Co–TMP and isomerized to **4e** and **4f** very slowly ($k_{3f\rightarrow 4f}/k_{3a\rightarrow 4a} \sim 1/60000$, by Co–TMP). Attack from the A direction should be more sensitive to the variation of steric hindrance around the axial sites of cobalt–porphyrin complexes. Suppression of the reactivity observed by intro-

(6) The k values in the isomerization of **1b** to **2b** by a cationic cobalt–porphyrin complex (cobalt 5,10,15,20-tetrakis(4-*N*-methylpyridyl)-porphyrin) was nearly equal to that in the isomerization by anionic ones (Co–TPPC or cobalt 5,10,15,20-tetrakis(*p*-sulfophenyl)porphyrin).[3a] Thus, coulombic interaction between the catalyst and the negatively charged quadricyclane species was not observed in aqueous solution involving a lot of salts.

(7) The porphyrin ring of Co–TPPC possesses 26 π-electrons and is substituted with four phenyl groups (24 π-electrons) at all the *meso* positions. Its hydrophilic carboxylate ions are remoter from the axial sites. Therefore, the tetraphenylporphyrin skeleton around the axial is relatively hydrophobic in an aqueous medium. The additivity of hydrophobicity of functional groups was already reported: Tomlinson, E. *J. Chromatogr.* **1975**, *113*, 1.

(8) Compound **1l** showed a little more bulkiness toward the A direction than **1k**, but **1l** reacted with Co–TPPC more rapidly than **1k**. The results may be explained as follows. Introduction of a methyl group to the three-membered ring of quadricyclanes reduced the thermal stability of the methylated quadricyclane derivative, which might also enhance the reactivity with a cobalt–porphyrin complex. This effect may affect k more largely than the weak steric effect. The results in **3a,b** may be explained similarly.

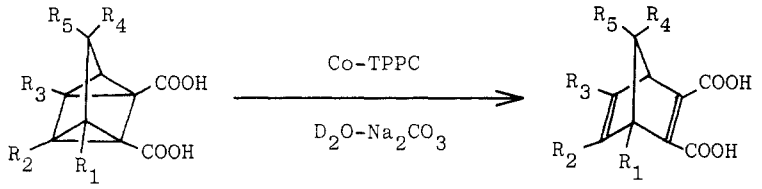
(9) Cassar, L.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1970**, 1082.

(10) Substitution with a single methyl group at the R_4 position of **3a** (as in **3d**) did not affect k; however, when a methyl group was already present at the R_5 position, the addition of a second methyl group at R_4 position caused a decrease in k of about 30% (compare **3e** with **3f**). This can be explained as follows: the methyl group at the R_5 position of **3f** may be more bulky toward the A direction than that of **3e** because of the steric repulsion between the two methyl groups at the R_4 and R_5 positions in **3f**.

(11) Recently, a similar observation in benzene was reported by: Yoshida, Z.; Ohno, T.; Iwasaki, H.; Miki, S. "Abstracts of Papers", 50th National Meeting of the Chemical Society of Japan, Tokyo, April 1985; Chemical Society of Japan: Tokyo, 1985; Abstr. No. 2O14.

(12) Bortolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1967.

Table III. Isomerization Rate Constant k^a in Aqueous Solution

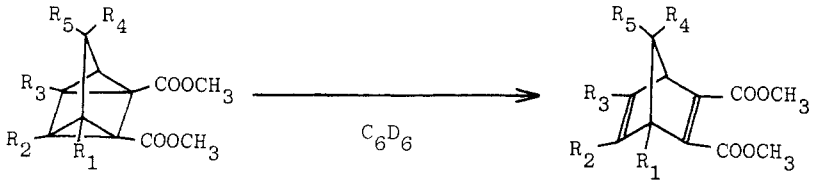


1k-o 2k-o

	R_1	R_2	R_3	R_4	R_5	$k/M^{-1}\ s^{-1}$
k	H	H	H	H	H	1×10
l	CH_3	H	H	H	H	4×10
m	H	CH_3	H	H	H	7×10^{-2}
n	H	CH_3	CH_3	H	H	$<5 \times 10^{-3}$
o	H	H	H	CH_3	H	2×10
p	H	H	H	H	CH_3	1×10^{-3}
q	H	H	H	CH_3	CH_3	9×10^{-4}

[a] Error was within ±15% (at 25 °C).

Table IV. Isomerization Rate Constant k^a in a Benzene Solution



3a-f (R_3=H) 4a-f (R_3=H)

					$k/M^{-1}\ s^{-1}$			
	R_1	R_2	R_4	R_5	Co-TPP	Co-TMP	Co-TPP-(*o*-Me)	Co-TPP-(*p*-Me)
a	H	H	H	H	12	12		
b	CH_3	H	H	H	21	13		
c	H	CH_3	H	H	0.33	0.036	0.23	0.33
d	H	H	CH_3	H	12	12		
e	H	H	H	CH_3	0.0037	0.0003_2		
f	H	H	CH_3	CH_3	0.0027	0.0002_1		

[a] Error was within ±15% (at 25 °C).

duction of methyl groups at the R_2 and R_5 positions of **3a** may be explained in this way. Consequently, in the isomerization of **1** to **2** in an aqueous alkaline solution, **1** might first enter into the hydrophobic field around the active sites of Co-TPPC to be attacked from the A direction, far from the hydrophilic carboxylate ion group in the molecule (Scheme IV).[13]

Experimental Section

Apparatus. All melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^1H NMR spectra were recorded on a JEOL JMN-PS-100 instrument; chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Ultraviolet and visible spectra were measured with a Shimadzu UV-200 spectrometer. Mass spectra were recorded with a JEOL JMS-DX-300 spectrometer. HPLC analyses were carried out with a JASCO liquid chromatograph containing a LiChrosorb RP-18 column. The elemental analyses were performed at the Microanalysis Center of Kyoto University.

Materials. Reagent-grade solvents were simply distilled and used. All acids, bases, and salts were commercially available and used without further purification. The compounds **1a–i**,[14] **2a–i**,[14] **1k**,[5a] **2k**,[15] **4a**[15] and **3a**[16] and the catalyst Co-TPPC[17] were synthesized according to the procedures given in the literature.

3-(Methoxycarbonyl)-2,5-norbornadiene-2-carboxylic Acid (2j). Methanol (0.41 mL; 10.0 mmol) was added dropwise to a dry acetone solution (10 mL) of 2,5-norbornadiene-2,3-dicarboxylic anhydride[14] (1.62 g; 10.0 mmol) at 0 °C. After being stirred for 1 h at 0 °C, the solution was concentrated in vacuo. The mixture was chromatographed over silica gel with benzene as an eluant. The ester **2j** was obtained as white needles in a yield of 73% (1.42 g), mp 108–109 °C. Recrystallization from dichloromethane and hexane gave an analytical pure sample: ^1H NMR ($CDCl_3$) δ 2.04–2.36 (2 H, m), 3.92 (3 H, s), 4.02–4.16 (1 H, m), 4.18–4.32 (1 H, m), 6.8–7.0 (2 H, m); IR (KBr) 2500–2800 (COOH), 1720, 1630 (C=O), 1600 cm^{-1} (C=C); MS, *m/e* 194 (M^+). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.82; H, 5.18.

Dimethyl 1-Methyl-2,5-norbornadiene-2,3-dicarboxylate (4b) and Dimethyl 5-Methyl-2,5-norbornadiene-2,3-dicarboxylate (4c). Dimethyl acetylenedicarboxylate (12.3 mL; 0.10 mol) was added to freshly distilled methylcyclopentadiene (8.1 g; 0.10 mol, a mixture of two isomers; 1-methylcyclopentadiene/2-methylcyclopentadiene = 1/1)[18] under nitrogen at 0 °C. After being stirred for 30 min and warmed up to 100 °C for 30 min, the reaction mixture was distilled.[15] A mixture (19.2 g; 86% yield) of the two isomers (**4b**/**4c** = 1/1) was obtained at 89–90 °C (0.7 mmHg). The isomers **4b,c** were separated by using reverse-phase liquid chromatography (RPLC) with water/methanol (1/1) as eluants. Distillation gave an analytically pure

(13) It is under investigation how the four-membered ring of **1** opens to give **2** after the approach of Co-TPPC on **1**.
(14) Maruyama, K.; Tamiaki, H.; Kawabata, S. *J. Org. Chem.* **1985**, *50*, 4742.
(15) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 236.
(16) Kaupp, G.; Prinzbach, H. *Helv. Chim. Acta* **1969**, *52*, 956.
(17) Maruyama, K.; Tamiaki, H.; Yanai, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 781.
(18) (a) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939. (b) McLean, S.; Haynes, P. *Ibid.* **1965**, *21*, 2313.

sample. **4b**: colorless oil; bp 90 °C (0.3 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.50 (3 H, s), 1.98–2.27 (2 H, m), 3.74 (3 H, s), 3.83 (3 H, s), 3.80–3.96 (1 H, m), 6.58–6.68 (1 H, m), 6.86–6.98 (1 H, m); IR (neat) 1735, 1720 (C=O), 1630, 1560 cm^{-1} (C=C); MS, *m/e* 222 (M^+). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.56; H, 6.44. **4c**: colorless oil; bp 92–93 °C (0.13 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.94 (3 H, d, *J* = 2 Hz), 2.04–2.32 (2 H, m), 3.68–3.86 (2 H, m), 3.80 (6 H, s), 6.24–6.35 (1 H, m); IR (neat) 1710 (C=O), 1630, 1615 cm^{-1} (C=C); MS, *m/e* 222 (M^+). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.61; H, 6.33.

1-Methyl-2,5-norbornadiene-2,3-dicarboxylic Acid (21). A methanol solution (10 mL) of the ester **4b** (0.84 g; 3.8 mmol) was added to a 10% sodium hydroxide aqueous solution (30 mL). The solution was refluxed overnight under nitrogen, condensed, cooled, acidified by aqueous HCl at 0 °C, and then extracted with ether. The extract was washed with brine and dried over $MgSO_4$, and the solvent was evaporated. The acid **2l** was obtained as white crystals in a yield of 94% (0.69 g): mp 97–99 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.67 (3 H, s), 2.01–2.35 (2 H, m), 3.98–4.10 (1 H, m), 6.61–6.71 (1 H, m), 6.86–6.97 (1 H, m), 11.25 (2 H, br); IR (KBr) 2250–2700 (COOH), 1695, 1610 (C=O), 1535 cm^{-1} (C=C); MS, *m/e* 194 (M^+). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.94; H, 5.10.

5-Methyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2m). In a manner similar to the synthesis of **2l**, the hydrolysis of the ester **4c** gave the acid **2m** in a yield of 97%: white needles; mp 118–120 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.96 (3 H, d, *J* = 4 Hz), 2.15–2.35 (2 H, m), 3.87–3.99 (1 H, m), 4.06–4.17 (1 H, m), 6.32–6.41 (1 H, m), 10.35 (2 H, br); IR (KBr) 2250–2700 (COOH), 1685, 1625, (C=O), 1560 cm^{-1} (C=C); MS, *m/e* 194 (M^+). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.96; H, 5.06.

Dimethyl *syn*-7-Methyl-2,5-norbornadiene-2,3-dicarboxylate (4d) and Dimethyl *anti*-7-Methyl-2,5-norbornadiene-2,3-dicarboxylate (4e). Dimethyl acetylenedicarboxylate (0.12 mL; 1.0 mmol) was added to a tetrahydrofuran solution of 5-methylcyclopentadiene[18] (~1 mmol) under nitrogen at −15 °C. After being stirred for 1 day, the solution was condensed and then distilled in vacuo. A mixture (56 mg; 25% yield) of the two isomers (**4d**/**4e** ~ 2/1) was obtained at 92–94 °C (0.18 mmHg). The isomers **4d,e** were separated by means of RPLC. **4d**: colorless oil; bp 93–94 °C (0.14 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.00 (3 H, d, *J* = 7 Hz), 2.79 (1 H, q, *J* = 7 Hz), 3.62–3.71 (2 H, m), 3.83 (6 H, s), 6.94–7.03 (2 H, m); IR (neat) 1705 (C=O), 1625 cm^{-1} (C=C); MS, calcd for $C_{12}H_{14}O_4$ *m/e* 222.0891, found *m/e* 222.0893 (M^+). **4e**: colorless oil; bp 91–93 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.92 (3 H, d, *J* = 6 Hz), 2.95 (1 H, q, *J* = 6 Hz), 3.64–3.72 (2 H, m), 3.81 (6 H, s), 6.72–6.80 (2 H, m); IR (neat) 1710 (C=O), 1620 cm^{-1} (C=C); MS, *m/e* 222 (M^+). Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.97; H, 6.42.

***syn*-7-Methyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2o).** In a manner similar to the synthesis of **2l**, the hydrolysis of the ester **4d** gave the acid **2o** in a yield of 93%: white crystals; mp 116–120 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 0.97 (3 H, d, *J* = 7 Hz), 2.84 (1 H, q, *J* = 7 Hz), 3.95 (2 H, m), 6.95 (2 H, m); IR (KBr) 2400–2680 (COOH), 1695, 1625 (C=O), 1585, 1560 cm^{-1} (C=C); MS, calcd for $C_{10}H_{10}O_4$ *m/e* 194.0578, found *m/e* 194.0575 (M^+).

***anti*-7-Methyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2p).** In a manner similar to the synthesis of **2l**, the hydrolysis of the ester **4e** gave the acid **2p** in a yield of 100%: white crystals; mp 172–174 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 0.96 (3 H, d, *J* = 6 Hz), 2.88 (1 H, q, *J* = 6 Hz), 3.94–3.97 (2 H, m), 6.72–6.76 (2 H, m); IR (KBr) 2300–2750 (COOH), 1695, 1625 (C=O), 1585, 1560 cm^{-1} (C=C); MS, calcd for $C_{10}H_{10}O_4$ *m/e* 194.0578, found *m/e* 194.0583 (M^+).

Dimethyl 7,7-Dimethyl-2,5-norbornadiene-2,3-dicarboxylate (4f). In the usual way, the reaction of 4,4-dimethyl-2-cyclopentenone[19] (2.1 g; 19.1 mmol) and lithium aluminum hydride in ether gave 4,4-dimethyl-2-cyclopentenol. To a benzene solution (80 mL) of the alcohol were added *p*-toluenesulfonic acid (~30 mg) and dimethyl acetylenedicarboxylate (1.3 mL; 10.6 mmol). The solution was refluxed for 2 days in a flask equipped with a Soxhlet extractor containing 3A molecular sieves under nitrogen. The solution was cooled, washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and then distilled. The ester **4f** was obtained in a yield of 98% (2.45 g): colorless oil; bp 80 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.15 (3 H, s), 1.22 (3 H, s), 3.44–3.52 (2 H, m), 3.76 (6 H, s), 6.72–6.80 (2 H, m); IR (neat) 1710 (C=O), 1625 cm^{-1} (C=C); MS, *m/e* 236 (M^+). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.11; H, 6.98.

7,7-Dimethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2q). In a manner similar to the synthesis of **2l**, the hydrolysis of the ester **4f** gave the acid **2q** in a yield of 96%: white needles; mp 137–139 °C (from dichloromethane and hexane); ^{1}H NMR ($CDCl_3$) δ 1.20 (6 H, s), 3.80–3.88 (2 H, m), 6.80–6.88 (2 H, m), 11.6 (2 H, br); IR (KBr) 2400–2700 (COOH), 1695, 1615 (C=O), 1580, 1560 cm^{-1} (C=C); MS, *m/e* 208 (M^+). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.42; H, 5.76.

5,6-Dimethyl-2,5-norbornadiene-2,3-dicarboxylic Acid (2n). According to the method described by A. Fishli et al.,[20] the reaction of 2-methyl-2-cyclopentenone[21] (0.96 g; 10.0 mmol) and methylmagnesium iodide in ether gave 2-methyl-2-cyclopentenol. To an ether solution (50 mL) of the alcohol were added *p*-toluenesulfonic acid (~20 mg) and dimethyl acetylenedicarboxylate (1.2 mL; 10.0 mmol) at 0 °C. After being stirred for 3 h at 0 °C and for 12 h at room temperature under nitrogen, the solution was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and then distilled. Dimethyl 5,6-dimethyl-2,5-norbornadiene-2,3-dicarboxylate[22] was obtained in a yield of 41% (965 mg): pale yellow oil; bp 120 °C (2 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.76 (6 H, s), 1.95–2.2 (2 H, m), 3.45–3.58 (2 H, m), 3.73 (6 H, s); IR (neat) 1710 (C=O), 1615 cm^{-1} (C=C); MS, calcd for $C_{13}H_{16}O_4$ *m/e* 236.1048, found *m/e* 236.1039 (M^+).

In a manner similar to the synthesis of **2l**, the hydrolysis of the ester gave the acid **2n** in a yield of 100%: pale yellow needles; mp 176–178 °C (from dichloromethane, in the dark); ^{1}H NMR (D_2O–Na_2CO_3) δ 2.31 (6 H, s), 2.36–2.66 (2 H, m), 3.9–4.0 (2 H, m); IR (KBr) 2250–2700 (COOH), 1680, 1625 (C=O), 1560 cm^{-1} (C=C); MS, *m/e* 208 (M^+). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.64; H, 5.89.

General Procedure for the Synthesis of Quadricyclane Derivatives. A dry acetonitrile solution of a norbornadiene derivative was prepared in Pyrex tubes under argon and was irradiated with a 300-W high-pressure mercury arc lamp. The completion of the photoreaction was determined by TLC, ^{1}H NMR, or HPLC techniques. In 0.01 M solutions of norbornadiene derivatives, typically, irradiation of about 1–6 h was required for the completion. The solvent was evaporated, and the residue was distilled or recrystallized to give a reasonably pure quadricyclane derivative. No byproduct was observed and the yield was nearly quantitative by means of ^{1}H NMR. Under neutral conditions, the free acids **1m,n** were thermally unstable, isomerizing to **2m,n** at ambient temperature, and had to be handled at lower temperatures, especially in an organic solvent.

3-(Methoxycarbonyl)quadricyclane-2-carboxylic acid (1j): white needles; mp 101–102 °C (from carbon tetrachloride); ^{1}H NMR ($CDCl_3$) δ 2.1–2.86 (6 H, m), 3.73 (3 H, s); IR (KBr) 2600–2750 (COOH), 1720, 1635 cm^{-1} (C=O); MS, *m/e* 194 (M^+). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.65; H, 5.16.

1-Methylquadricyclane-2,3-dicarboxylic acid (1l): white plates; mp >300 °C (from dichloromethane and hexane); ^{1}H NMR (D_2O–Na_2CO_3) δ 1.47 (3 H, s), 2.32–2.50 (4 H, m), 2.71–2.83 (1 H, m); IR (KBr) 2350–2750 (COOH), 1670, 1610 cm^{-1} (C=O); MS, calcd for $C_{10}H_{10}O_4$ *m/e* 194.0578, found *m/e* 194.0584 (M^+).

5-Methylquadricyclane-2,3-dicarboxylic acid (1m): white crystals; ^{1}H NMR (D_2O–Na_2CO_3) δ 1.47 (3 H, s), 2.05–2.58 (5 H, m); IR (KBr) 2350–2700 (COOH), 1695, 1615 cm^{-1} (C=O); MS, calcd for $C_{10}H_{10}O_4$ *m/e* 194.0578, found *m/e* 194.0578 (M^+).

5,6-Dimethylquadricyclane-2,3-dicarboxylic acid (1n):

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white crystals; ^{1}H NMR (D_2O–Na_2CO_3) δ 1.8–2.08 (2 H, m), 1.9 (6 H, s), 2.44–2.64 (2 H, m); IR (KBr) 2400–2700 (COOH), 1695, 1615 cm^{-1} (C=O); MS, calcd for $C_{11}H_{12}O_4$ m/e 208.0753, found m/e 208.0737 (M^+).

***syn*-7-Methylquadricyclane-2,3-dicarboxylic acid (1o)**: white crystals; mp 218–222 °C (from dichloromethane and hexane); ^{1}H NMR (D_2O–Na_2CO_3) δ 1.27 (3 H, d, J = 6 Hz), 2.24 (2 H, d, J = 5 Hz), 2.44 (2 H, d, J = 5 Hz), 2.74 (1 H, q, J = 6 Hz); IR (KBr) 2400–2650 (COOH), 1685, 1615 cm^{-1} (C=O); MS, calcd for $C_{10}H_{10}O_4$ m/e 194.0578, found m/e 194.0578 (M^+).

***anti*-7-Methylquadricyclane-2,3-dicarboxylic acid (1p)**: white crystals; mp 160–163 °C (from ether); ^{1}H NMR (D_2O–Na_2CO_3) δ 1.05 (3 H, d, J = 7 Hz), 1.92 (2 H, d, J = 5 Hz), 2.39 (2 H, d, J = 5 Hz), 2.76 (1 H, q, J = 7 Hz); IR (KBr) 2400–2700 (COOH), 1690, 1625 cm^{-1} (C=O); MS, calcd for $C_{10}H_{10}O_4$ m/e 194.0578, found m/e 194.0581 (M^+).

7,7-Dimethylquadricyclane-2,3-dicarboxylic acid (1q): white crystals; mp 237–239 °C (from dichloromethane and hexane); ^{1}H NMR (D_2O–Na_2CO_3) δ 1.26 (3 H, s), 1.37 (3 H, s), 1.84 (2 H, d, J = 5 Hz), 2.39 (2 H, d, J = 5 Hz); IR (KBr) 2350–2700 (COOH), 1675, 1600 cm^{-1} (C=O); MS, calcd for $C_{11}H_{12}O_4$ m/e 208.0735, found m/e 208.0734 (M^+).

Dimethyl 1-methylquadricyclane-2,3-dicarboxylate (3b): colorless oil; bp 105 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.29 (3 H, s), 2.06–2.54 (5 H, m), 3.66 (3 H, s), 3.74 (3 H, s); IR (neat) 1715 cm^{-1} (C=O); MS, calcd for $C_{12}H_{14}O_4$ m/e 222.0891, found m/e 222.0892 (M^+).

Dimethyl 5-methylquadricyclane-2,3-dicarboxylate (3c): colorless oil; bp 110 °C (0.15 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.41 (3 H, s), 2.08–2.37 (5 H, m), 3.66 (3 H, s), 3.68 (3 H, s); IR (neat) 1725, 1705 cm^{-1} (C=O); MS, calcd for $C_{12}H_{14}O_4$ m/e 222.0891, found m/e 222.0889 (M^+).

Dimethyl *syn*-7-methylquadricyclane-2,3-dicarboxylate (3d): colorless oil; bp 102–105 °C (0.16 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.29 (3 H, d, J = 7 Hz), 2.10–2.21 (2 H, m), 2.49 (2 H, d, J = 5 Hz), 2.69 (1 H, q, J = 7 Hz), 3.76 (6 H, s); IR (neat) 1705 cm^{-1} (C=O); MS, calcd for $C_{12}H_{14}O_4$ m/e 222.0891, found m/e 222.0891 (M^+).

Dimethyl *anti*-7-methylquadricyclane-2,3-dicarboxylate (3e): colorless oil; bp 110 °C (0.2 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.08 (3 H, d, J = 6 Hz), 2.12–2.26 (2 H, m), 2.54 (2 H, d, J = 4 Hz), 2.85 (1 H, q, J = 6 Hz), 3.70 (6 H, s); IR (neat) 1720 cm^{-1} (C=O); MS, calcd for $C_{12}H_{14}O_4$ m/e 222.0891, found m/e 222.0890 (M^+).

Dimethyl 7,7-dimethylquadricyclane-2,3-dicarboxylate (3f): white crystals; bp 95 °C (0.2 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.21 (3 H, s), 1.30 (3 H, s), 1.97 (2 H, d, J = 5 Hz), 2.50 (2 H, d, J = 5 Hz), 3.69 (6 H, s); IR (neat) 1725, 1710 cm^{-1} (C=O); MS, calcd for $C_{13}H_{16}O_4$ m/e 236.1048, found m/e 236.1053 (M^+).

Co-TPP. According to the method described by A. D. Adler et al.,[23] the reaction of H_2-TPP[24] and cobalt acetate ($Co(OAc)_2$) in dimethylformamide (DMF) gave Co-TPP. Chromatography over silica gel with dichloromethane and hexane as eluants and recrystallization from dichloromethane and methanol gave an analytically pure sample: reddish purple crystals; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 9.72 (4 H, m), 9.92 (8 H, m), 13.1 (8 H, br), 15.9 (8 H, br); UV (C_6H_6) λ_{max} 413 (ϵ 271 000), 529 nm (16 700). Anal. Calcd for $C_{44}H_{28}N_4Co$: C, 78.68; H, 4.20; N, 8.34. Found: C, 78.42; H, 4.03; N, 8.31.

Co-TPP(*o*-Me). In a manner similar to the synthesis of Co-TPP, the reaction of H_2-TPP(*o*-Me)[25] and $Co(OAc)_2$ in DMF gave Co-TPP(*o*-Me) as a mixture of atropisomers: purple plates; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 2.4, 3.2, 3.9, and 4.6 (12 H, br, *o*-CH_3), 9.2–9.9 (12 H, m, meta and para H), 11.7, 12.3, 12.9, and 13.5 (4 H, br, ortho H), 15.4 (8 H, br, pyrrole H); UV (C_6H_6) λ_{max} 412 (ϵ 253 000), 528 nm (15 400). Anal. Calcd for $C_{48}H_{36}N_4Co$: C, 79.22; H, 4.99; N, 7.70. Found: C, 79.18; H, 5.00; N, 7.70.

Co-TPP(*p*-Me). In a manner similar to the synthesis of Co-TPP, the reaction of H_2-TPP(*p*-Me)[24] and $Co(OAc)_2$ in DMF gave Co-TPP(*p*-Me): purple needles; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 4.14 (12 H, s), 9.73 (8 H, m), 13.0 (8 H, br), 15.9 (8 H, br); UV (C_6H_6) λ_{max} 414.5 (ϵ 272 000), 530 nm (16 500). Anal. Calcd for $C_{48}H_{36}N_4Co$: C, 79.22; H, 4.99; N, 7.70. Found: C, 79.08; H, 4.84; N, 7.68.

Co-TMP. In a manner similar to the synthesis of Co-TPP, the reaction of H_2-TMP[26] and $Co(OAc)_2$ in DMF gave Co-TMP: reddish purple crystals; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 1.52 (24 H, s), 3.92 (12 H, s), 9.18 (8 H, s), 15.2 (8 H, br); UV (C_6H_6) λ_{max} 412.5 (ϵ 260 000), 528.5 nm (16 500). Anal. Calcd for $C_{56}H_{52}N_4Co$: C, 80.07; H, 6.24; N, 6.67. Found: C, 80.06; H, 6.34; N, 6.75.

Measurement of Second-Order Rate Constants. According to the literature,[3a] the rate constants were determined by means of ^{1}H NMR ([1] = 0.1 M, in 0.5 M Na_2CO_3–D_2O, at 25 °C; [3] = 0.1 M, in C_6D_6, at 25 °C).

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$S_{RN}1$ Reactions of Halocyclopropanes with Benzenethiolate Ion

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Ultraviolet irradiation of *gem*-dibromocyclopropanes **1** with benzenethiolate ion in liquid ammonia or in Me_2SO solution gave dithioacetals **2** and, in some cases, cyclopropyl phenyl sulfides **3**. The reactions did not proceed in the dark and they were inhibited by *m*-dinitrobenzene, di-*tert*-butyl nitroxide, and oxygen. The bromocyclopropane **6a** underwent a similar, but slower, reaction. Treatment of the bromochlorocyclopropane **7b** led to replacement of only the bromine, while the dichlorocyclopropane **9b** was inert under the reaction conditions. The results appear consistent with a radical chain mechanism.

Nucleophilic substitution of *gem*-dihalocyclopropanes normally involves an elimination–addition sequence and in many cases the nucleophile enters *cine* to the leaving group.[1] Attempted substitution by the S_N1 mechanism usually leads to fissure of the ring,[2,3] whereas substitution by the S_N2 mechanism is considered geometrically unfavorable.[5,6]

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