Conformational Locking by Intramolecular Hydrogen Bonding and Unlocking by Solvation Using 7-Vinylnorcaradienes

Shigeo Kohmoto,* Ichiro Koyano, Teruyuki Kawatsuji, Hideaki Kasimura,† Keiki Kishikawa, Makoto Yamamoto, and Kazutoshi Yamada

Department of Materials Science, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263

†Central Customs Laboratory, Ministry of Finance, Matsudo, Chiba 271

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Norcaradiene derivatives **1**, 5-(1-benzyloxycarbonyl-2-methyl-1-propenyl)-3-oxatricyclo[4.4.0.0^{1,5}]deca-7,9-dien-4-one, showed a restricted rotation in the ^{1}H NMR spectra. VT ^{1}H NMR measurements in $CDCl_3$ revealed the existence of two rotamers at low temperature with $\Delta G^{\neq}$ of 11.5 (250 K), 12.1 (263 K), and 13.9 kcal mol^{-1} (296 K) for norcaradienes with R = H, Me, and *t*-Bu, where R is the para substituent of the benzyloxy group, respectively. This restricted rotation was stopped in $CDCl_3$ at ambient temperature by introducing intramolecular hydrogen bonding via reducing of the lactone moiety to the corresponding lactols. The observed conformational locking due to the intramolecular hydrogen bonding was unlocked by solvation, resulting in the formation of three conformers in methanol-d_4 and dimethyl-d_6 sulfoxide. VT ^{1}H NMR measurements of the lactol derivative in dimethyl-d_6 sulfoxide showed that two of the conformers interconverted with $\Delta G^{\neq}$ of 17.4 kcal mol^{-1}.

Hydrogen bonding is an important major force in molecular recognition to fix the geometry of molecules in a proper position,[1] though it is not strong enough to stop conformational changes of molecules at ambient temperature in solution by a single hydrogen bonding (2—10 kcal mol^{-1}).[2] It requires a rotational barrier of 22.3 kcal mol^{-1} minimum (half-life of 1000 s, rotamer ratio of 1 : 1) at 300 K for rotamers to be isolated.[3] In a restricted rotation around a σ-bond with a $\Delta G^{\neq}$ of $(22.3-x)$ kcal mol^{-1} for example, the summation of an additional energy barrier of x kcal mol^{-1} to the system can stop this rotation at ambient temperature. This can possibly be achieved by introducing intramolecular hydrogen bonding as the source of an additional energy barrier. The hydrogen bonding can selectively hold one of the rotamers, depending on its geometrical location. Moreover, this conformational locking can be unlocked by solvation in a polar protic solvent.

During the preparation of 1,7-lactol ring-fused norcaradiene **3a**[4] for its acid-catalyzed dehydrative amortization reaction, as a part of our study of stable norcaradienes,[5,6] we noticed a different ^{1}H NMR behavior between **3a** and the corresponding γ-lactone derivative **1a** (Chart 1). This difference depends on the presence (in **1a**) or the absence (in **3a**) of the restricted rotation around the C^5–C^a single bond at ambient temperature. In this report, we demonstrate the above-mentioned idea of conformational locking and unlocking in this norcaradiene system using intramolecular hydrogen bonding and solvation, respectively.

Results and Discussion

The ^{1}H NMR spectra of norcaradienes **1** in $CDCl_3$ at ambient temperature showed broad signals. Since the proton and carbon chemical shifts of H^6, C^1, and C^6 are typical values of norcaradienes,[7] the observed broadening is not caused by a norcaradiene–cycloheptatriene eqilibrium, but is the result of restricted rotation around the C^5–C^a single bond in the norcaradiene structure. This restricted rotation originates from a steric repulsion between the ester substituent at C^a and the cyclohexadiene moiety, since the less-bulky norcaradiene **2**[6] does not show restricted rotation. The intensity of the steric hindrance between them was increased in proporion to the bulkiness of substituent(R). Substitution with bulky groups increased the number of broadening of the signals. In **1a** (R = H), only H^{10} appears as a broad signal among vinylic cyclohexadiene ring protons. The introduction of a methyl group at C^8 (**1b**) caused a broadening of the methyl group at C^8, two vinylic protons H^{10} and H^7, and geminal protons H^2. Substitution with a *t*-Bu group at C^8 resulted in an additional broadening of H^9 and the vinylic *gem*-dimethyl group.

The VT ^{1}H NMR experiment revealed the detailed process of the exchange of two conformers at low temperature. Figure 1 shows the temperature-dependent ^{1}H NMR spectra of protons H^2 and H^6 of **1b** in $CDCl_3$ as a representative example. The geminal protons H^2 appeared together as a broad peak at $\delta = 4.03$ at 292 K. They gradually broadened and separated into two sets of two doublet peaks with $J = 9.6$ Hz at 220 K. Similarly, H^6 separated into two doublet peaks with $J = 4.6$ Hz. The major rotamer might have a conformation corresponding to the rotamer **A** in which the phenyl ring shields H^2 to cause an upfield shift of ca. 0.6 ppm. The chemical shift of H^2 of the minor rotamer has quite similar values to those of norcaradiene **2** ($\delta = 4.55$ and 4.32 with $J = 10.0$

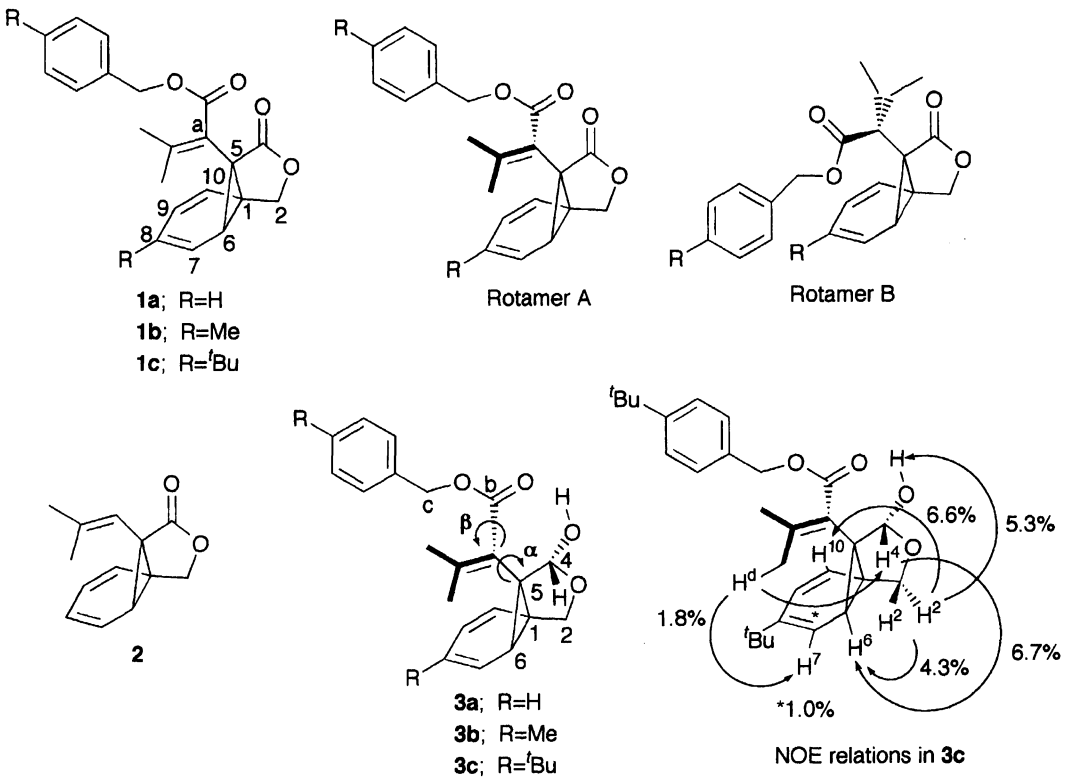

Chart 1.

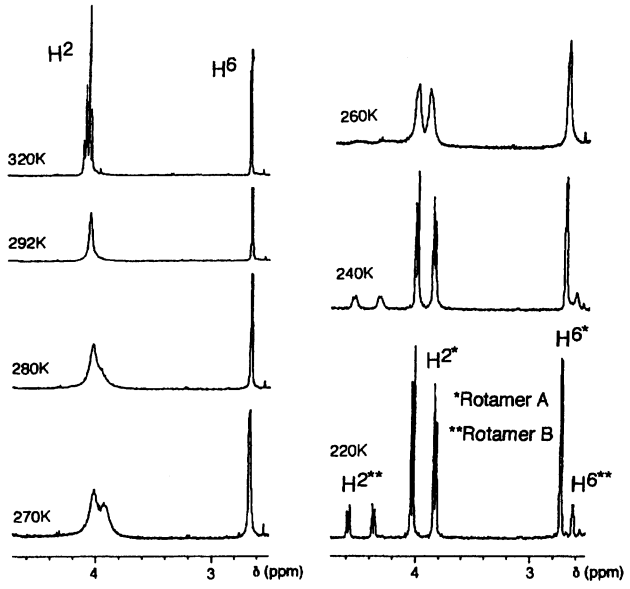

Fig. 1. Variable temperature ^{1}H NMR spectrum of **1b** (protons H^2 and H^6) in $CDCl_3$.

Hz in $CDCl_3$), which indicates the lack of a shielding effect by the phenyl group in this conformation. Therefore, the minor rotamer should have a conformation corresponding to the rotamer **B**. The conformation of the rotamer **A** is identical to that found in the crystal structure of **1a**.[5] Approximate rotational barriers for **1a**—**c** were estimated to be $\Delta G^{\neq}$ of 11.5, 12.1, and 13.9 kcal mol^{-1} at coalescence temperatures of 250, 263, and 296 K, respectively.[8] The rotamer ratios were 8 : 1, 4 : 1, and 5 : 1 for **1a**, **1b**, and **1c**, respectively at 220 K in $CDCl_3$.

In order to add an additional barrier to the rotation around the C^5–C^a single bond, a diisobutylaluminium hydride (DIBALH) reduction of **1a**—**c** was carried out to give the corresponding lactols **3a**—**c** in yields (conversion yields) of 87, 81, and 86%, respectively. The reduction was regio and stereoselective to give a single diastereomer. Since **2** was reduced by DIBALH to give the diastereomeric lactols,[4] the stereoselective reduction of **1** might be caused by the effect of the benzyloxycarbonyl group, which might contribute to the coordination of aluminum kinetically more preferable in rotamer **A** than in rotamer **B**. Thus, the attack of hydride from the front side (the C^6 side) in rotamer **A** gave **3**. Unlike the ^{1}H NMR spectra of **1a**—**c**, those of **3a**—**c** in $CDCl_3$ showed sharp signals at 292 K. The NOE relations from NOE difference spectroscopy, as exemplified for **3c**, unequivocally determine the stereochemistry of the hydroxy group and the conformation of the C^5 substituent. The NOE enhancement between protons H^4 and H^d (the olefinic methyl proton) shows that these protons are at the same side of the molecule. Therefore, the hydroxy and benzyloxycarbonyl groups are located on the same side. An observation of coupling between H^4 and hydroxy proton (J = 11.3, 11.3, and 11.6 Hz for **3a**, **3b**, and **3c**, respectively) indicated a fixed geometry of hydroxy group by intramolecular hydrogen bonding with the carbonyl of the benzyloxycarbonyl group. This coupling disappeared upon the addition of D_2O. The existence of intramolecular hydrogen bonding was also confirmed from their IR spectra; ν_{OH} appeared at 3350 cm^{-1}

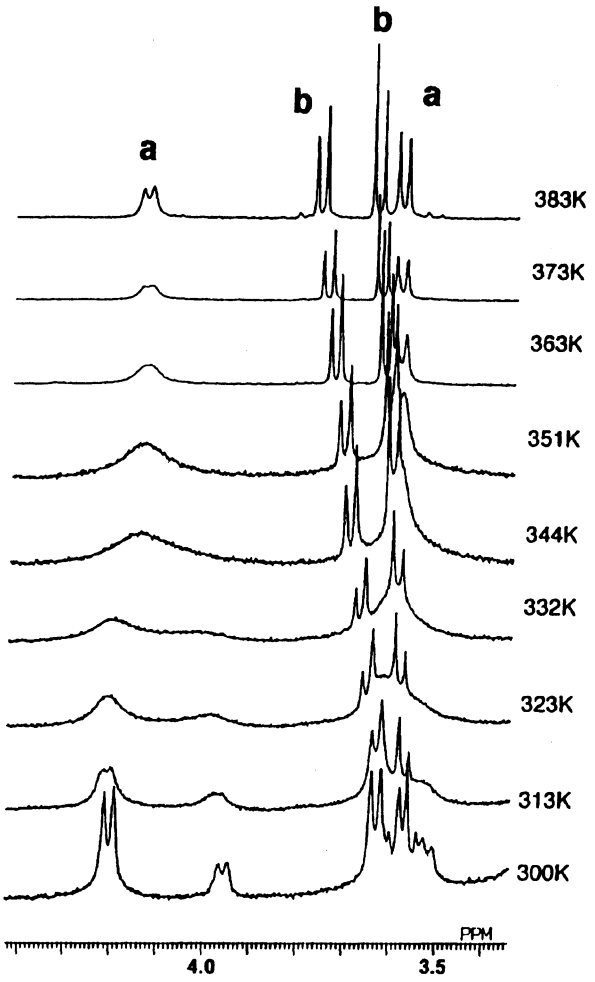

Fig. 2. Variable temperature ^{1}H NMR spectrum of **3a** (proton H^2) in DMSO-d_6. Three conformers observed at 300 K were coalesced at 351 K and two conformers (**a** and **b**) were observed at 383 K.

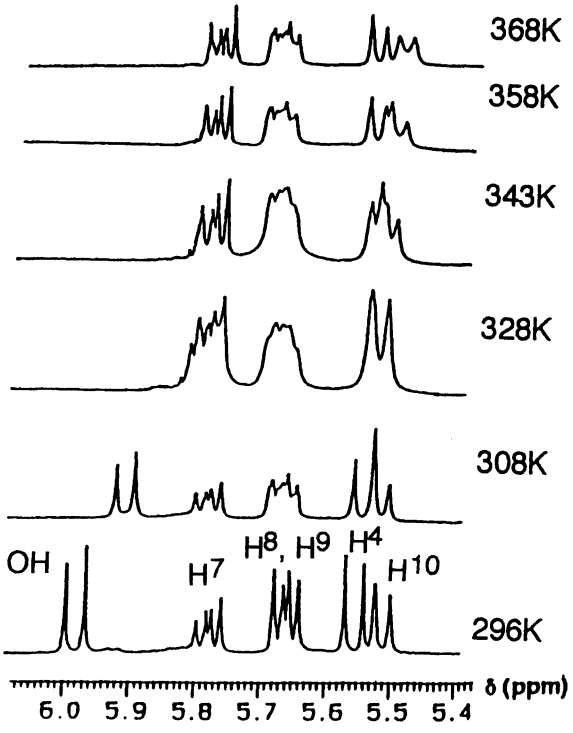

Fig. 3. Variable temperature ^{1}H NMR spectrum of **3a** in toluene-d_8.

for **3a** and **3b**, and 3408 cm^{-1} for **3c**. Thus, this hydrogen bonding affords an additional rotational barrier that is sufficient to stop the occurrence of restricted rotation, and to fix their conformation selectively to that corresponding to the major rotamer of **1**. Since the rotational barriers for **1a**—**1c** are in the range of 11.5 to 13.9 kcal mol^{-1}, the additional barrier (x) gained by the intramolecular hydrogen bonding is about 8—11 kcal mol^{-1}.

In contrast to the NMR spectrum of **3a**—**c** in $CDCl_3$, those in methanol-d_4 and dimethyl-d_6 sulfoxide resulted in totally different spectra. In the ^{1}H NMR spectra of **3b** in methanol-d_4 at ambient temperature, three sets of signals were observed for H^6, H^4, and H^2. Similar spectral changes were observed for **3a** and **3c**. However, due to the complexity of the spectra, some of the peaks overlapped. Three sets of carbon signals were also observed in their ^{13}C NMR spectra, especially for C^1, C^6, C^5, and C^4, which showed that the norcaradiene and lactol structures remained. Therefore, three norcaradiene conformers should exist. The characteristic ^{13}C and ^{1}H NMR chemical shifts of three comformers for **3a**—**c** are summarized in Table 1. The breaking of hydrogen bonding by solvation with methanol allows rotation around single bonds. The three energy minima in the solvated form may be due to a restriction of two rotations around the single bonds α and β. The former restricted rotation may create two stable conformations similar to rotamer **A** and **B**. In one of them, the second rotation around single bond β may be restricted to give two stable conformations, which result in a total of three stable conformations. These spectral changes were reversible when the solvent was changed back to $CDCl_3$ from methanol-d_4. The results indicate that the conformational locking with intramolecular hydrogen bonding is unlocked by solvation with methanol, affording three conformers. Similarly, three conformers were observed in dimethyl-d_6 sulfoxide. The protons H^2 appeared as three sets of two doublet peaks. The ^{1}H NMR VT experiments of **3a** (Fig. 2) showed that two of the conformers coalesced at 351 K with $\Delta G^{\neq}$ of 17.4 kcal mol^{-1}. The existence of two conformers was confirmed from the two sets of two doublet peaks for geminal protons H^2 observed at 383 K. The rotation around the C^5–C^a bond was estimated to be over 19 kcal mol^{-1}. The existence of an equilibrium between the two conformers out of three was also confirmed by magnetization transfer in an NOE difference spectrum of **3a** in methanol-d_4. The irradiation of the proton H^2 of the major conformer caused an enhancement of the proton H^2 corresponding to one of the other conformers.

In order to release the frozen rotation by intramolecular hydrogen bonding in a nonpolar solvent, the VT ^{1}H NMR experiment of **3a** in toluene-d_8 was investigated. The ^{1}H NMR spectrum of **3a** in toluene-d_8 at 296 K showed sharp signals as its spectrum in $CDCl_3$. According to the increase in

Table 1. Selected $^{13}C^{a)}$ and $^{1}H^{b)}$ NMR Chemical Shift (δ) of Three Conformers of **3a**—**c** in Methanol-d_4

Carbopn	**3a**	**3b**	**3c**	Proton	**3a**	**3b**	**3c**
C^1	26.95	27.55	26.20				
	26.73	27.11	26.05				
	26.60	26.90	25.75				
C^6	38.73	37.16	35.48	H^6	2.33 (d, J=5.5 Hz)	2.22 (d, J=5.2 Hz)	2.25 (d, J=5.5 Hz)
	36.80	35.34	34.35		2.68 (d, J=5.5 Hz)	2.58 (d, J=5.4 Hz)	2.60 (d, J=5.2 Hz)
	34.95	33.09	34.32			1.79 (d, J=5.1 Hz)	
C^5	45.55	44.26	42.54				
	44.78	42.30	40.05				
	43.68	41.16	39.87				
C^4	105.75	104.90	103.78	H^4		5.32 (s)	
	104.47	103.60	102.43			5.75 (s)	
	102.31	101.41	100.18			5.50 (s)	
C^2	71.88	71.08	69.83	H^2	4.12 (d, J=8.1 Hz)	4.08 (d, J=8.4 Hz)	4.11 (d, J=8.4 Hz)
	71.42	70.51	69.41		3.62 (d, J=8.1 Hz)	3.61 (d, J=8.4 Hz)	3.61 (d, J=8.4 Hz)
&	70.85	69.94	68.62				
	68.85	67.89	66.74		3.76 (d, J=8.1 Hz)	3.77 (d, J=8.4 Hz)	
	67.98	67.84	65.72		3.65 (d, J=8.1 Hz)	3.65 (d, J=8.4 Hz)	
C^c	67.81	66.91	65.59				
C^b	173.74	173.02	172.47		4.36 (d, J=8.1 Hz)	4.33 (d, J=8.4 Hz)	4.35 (d, J=8.4 Hz)
	170.72	170.35	168.47		3.73 (d, J=8.1 Hz)	3.72 (d, J=8.4 Hz)	3.72 (d, J=8.4 Hz)
	170.34	169.82					

a) Three ^{13}C peaks for each carbon were observed except for C^b of **3c** in which two of them was overlapped. Chemical shift of the peaks were tabulated from the lower field peak. b) Some of the peaks could not be assigned due to the overlap with other peaks. Ratios of three conformers were determined to be 2 : 2 : 1, 2 : 1 : 1, and 6 : 3 : 1 for **3a**, **3b**, and **3c** respectively.

the measurement temperature (Fig. 3), a broadening of the peaks was observed, except for geminal protons H^2, which indicated that these two protons escaped from the influence of the rotation of the 5-vinyl group. The broadened peaks due to the initiation of the restricted rotation became sharper at higher temperature (368 K). The results indicated that free rotations around the α and β bonds began to occur. The small chemical shift change for proton H^6 (δ = 2.12 at 296 K and δ = 2.14 at 368 K) suggested that **3a** maintained the norcaradiene structure even at 368 K. At temperatures higher than 383 K, thermal rearrangements of **3a**, (vinylcyclopropane–cyclopentene rearrangement and Cope rearrangement[9]) took place. The observed spectral changes (up to 368 K) were reversible when the sample solution was cooled down to 296 K.

As we have shown, the introduction of an additional rotational barrier by intramolecular hydrogen bonding to a system involving a restricted rotation can lock the conformation of molecules. It has shown that unlocking it can be achieved by solvation.

Experimental

General. The melting points were determined on a Yanako MP-S3 melting-point apparatus and are uncorrected. IR spectra were obtained in a JASCO A-202 spectrometer. NMR spectra were recorded on JOEL FX-90, JNM FX-270 or GSX-400 spectrometers in $CDCl_3$ with Me_4Si as an internal standard; J values are given in Hz. Mass spectra were obtained on a JEOL JMS-HX110 mass spectrometer. Elemental analyses were performed on a Perkin–Elmer 240 analyzer. Reaction mixtures were concentrated on a rotary evaporator at 15—20 mmHg (1 mmHg = 133.322 Pa). Chromatographic separations were accomplished by flash column chromatography on silica gel (Fuji gel BW 200). Further purification of products was carried out by a preparative HPLC run; column Merck LiChrosorb Si60 (7 μm 10× 250 mm), hexane/ethyl acetate as eluent.

Procedure for Preparation of 1c. The reported method for **1a** and **1b**[5] was employed. A solution of 3*H*-pyrazole (310 mg, 0.651 mmol) in benzene (15 ml) prepared from the reaction of bis(*p*-*t*-butylbenzyl) acetylenedicarboxylate and 2-diazopropane in a Pyrex test tube was irradiated for 50 min under an argon atmosphere with a 400-W high-pressure mercury lamp. The color of the reaction solution was changed from colorless to yellow, and finally to colorless during irradiation. After removing the solvent, toluene (6 ml) was added to the residue, and the resulting mixture was thermolyzed in a sealed tube for 15.5 h at 130 °C. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel with hexane–ethyl acetate (3 : 1) as an eluent. Further purification by recrystallization gave **1c** (134 mg, 46%).

(1*RS*, 5*SR*, 6*RS*)-5[1-(*p*-*t*-Butylbenzyloxycarbonyl)-2-methyl-1-propenyl]-8-*t*-butyl-3-oxatricyclo[4.4.0.0^{1,5}]deca-7,9-dien-4-one (1c): Colorless needles; mp 140—141 °C; MS (*m*/*z*) 448 (M^+ ; 5%), 301 (20), 284 (17), 148 (65), 147 (100), 132 (70), 117 (60), 105 (25), 91 (30); IR ($CHCl_3$) 3030, 2970, 2910, 1760, 1640, 1370, 1280-1195, 1080, 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ = 1.00 (9H, s), 1.32 (9H, s), 2.00 (3H, br.s), 2.01 (3H, s), 2.70 (1H, d, J = 5.4 Hz), 3.98 (2H, br.m), 4.94 (1H, br.d, J = 12.3 Hz), 5.09 (1H, d, J = 12.3 Hz), 5.44 (1H, br.d, J = 9.6 Hz), 5.82 (1H, br.), 6.05 (1H, d, J = 9.6 Hz), 7.32 (2H, d, J = 7.7 Hz), 7.41 (2H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 22.4 MHz) δ = 22.32 (q), 22.75 (s), 23.74

(q), 29.19 (q), 31.32 (q), 34.16 (s), 34.62 (s), 39.12 (d), 39.75 (d), 65.91 (t), 70.49 (t), 112.95 (d), 116.39 (s), 121.41 (d), 124.76 (d), 125.46 (d), 128.56 (d), 132.85 (s), 146.89 (s), 151.54 (s), 157.47 (s), 166.34 (s), 177.75 (s). Found: C, 77.58; H, 8.14%. Calcd for $C_{29}H_{36}O_4$: C, 77.64; H, 8.09%.

Procedure for Preparation of 3. To a solution of **1a** (70.0 mg, 0.208 mmol) in dry toluene (6 ml) was added a hexane solution (0.93 M, 1 M = 1mol dm^{-3}) of DIBALH (0.36 ml, 0.33 mmol) at −78 °C. After stirring for 3 h at −78 °C, ethyl acetate (15 ml) was added to the reaction mixture; water (10 ml) was then added at −5 °C. The aqueous layer was extracted with ethyl acetate (5 ml × 3). The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation, and the residue was purified by column chromatography. Further purification by HPLC (hexane : ethyl acetate = 4 : 1 as eluent) gave **3a**[4] (49.0 mg, 70%, conversion yield 87%) together with recovered **1a** (14.0 mg, 20%). In a similar manner, **3b** (21.0 mg, 40%, conversion yield 81%) and **3c** (45.9 mg, 55%, conversion yield 86%) were obtained from **1b** (52.1 mg, 0.143 mmol) and **1c** (83 mg, 0.185 mmol), respectively.

(1*RS*, 4*SR*, 5*SR*, 6*RS*)-8-Methyl-5-[2-methyl-1-(*p*-methylbenzyloxycarbonyl)-1-propenyl]-3-oxatricyclo[4.4.0.0^{1,5}]deca-7,9-dien-4-ol (3b): IR ($CHCl_3$) 3350, 3000, 1720, 1665, 1280, 1225, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.75 (3H, s), 1.84 (3H, s), 1.93 (3H, s), 2.29 (1H, d, J = 5.3 Hz), 2.36 (3H, s), 3.69 (1H, d, J = 8.3 Hz), 4.13 (1H, d, J = 8.3 Hz), 5.06 (2H, s), 5.39 (1H, d, J = 11.3 Hz), 5.59—5.69 (3H, m), 5.84 (1H, d, J = 11.3 Hz, exchanged with D_2O), 7.18 (2H, d, J = 7.6 Hz), 7.24 (2H, d, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 22.4 MHz) δ = 21.15 (q), 21 .36 (q), 22.40 (q), 22.67 (q), 25.89 (s), 35.83 (d), 39.83 (s), 66.74 (t), 68.80 (t), 100.21 (d), 117.13 (d), 119.01 (s), 121.07 (d), 127.36 (d), 128.70 (d), 128.85 (s), 129.24 (d), 132.22 (s), 138.34 (s), 152.42 (s) 171.40 (s). HRMS (FAB): Found: *m/z* 405.1475 MK$^+$. Calcd for $C_{23}H_{26}O_4K$: MK, 405.1468.

(1*RS*, 4*SR*, 5*SR*, 6*RS*)-5-[1-(*p*-*t*-Butylbenzyloxycrbonyl)-2-methyl-1-propenyl]-8-*t*-butyl-3-oxatricyclo[4.4.0.0^{1,5}]deca-7,9-dien-4-ol (3c): IR (NaCl) 3408, 2958, 1719, 1676, 1208, 1079 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.94 (9H, s), 1.32 (9H, s), 1.84 (3H, s), 1.93 (3H, s), 2.31 (1H, d, J = 5.4 Hz), 3.72 (1H, d, J = 8.2 Hz), 4.18 (1H, d, J = 8.2 Hz), 5.00 (1H, d, J = 11.6 Hz), 5.18 (1H, d, J = 11.6 Hz), 5.41 (1H, d, J = 11.6 Hz), 5.64 (1H, br.d, J = 9.8 Hz), 5.77 (1H, br.d, J = 5.4 Hz), 5.79 (1H, dd, J = 9.8, 1.5 Hz), 6.05 (1H, d, J = 11.6 Hz, exchanged with D_2O), 7.30 (2H, d, J = 7.5 Hz), 7.40 (2H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 22.4 MHz) δ = 22.49 (q), 22.76 (q), 26.07 (s), 29.32 (q), 31.26 (q), 33.89 (s), 34.61 (s), 35.32 (d), 39.80 (s), 66.71 (t), 68.71 (t), 100.21 (d), 113.40 (d), 119.19 (s), 121.07 (d), 124.14 (d), 125.36 (d), 128.94 (d), 132.08 (s), 145.05 (s), 151.74 (s), 152.00 (s), 171.85 (s). HRMS (FAB): Found: *m/z* 489.2406 MK$^+$. Calcd for $C_{29}H_{38}O_4K$: MK, 489.2407.

References

1) a) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990); b) M. C. Etter, *Acc. Chem. Res.*, **23**, 120 (1990); c) J. Rebek, Jr., *Acc. Chem. Res.*, **23**, 399 (1990); d) J. Rebek, Jr., *Angew. Chem., Int. Ed. Engl.*, **29**, 245 (1990); e) G. A. Jeffrey and W. Saenger, "Hydrogen Bonding in Biological Structures," Springer-Verlag, Berlin (1991); f) H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **30**, 1417 (1991); g) C. Seel and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **31**, 528 (1992); h) R. Hoss and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, **33**, 375 (1994); i) M. Kotera, J.-M. Lehn, and J.-P. Vigneron, *Tetrahedron*, **51**, 1953 (1995).

2) N. S. Isaacs, "Physical Organic Chemistry, " Longman Scientific & Technical, Essex (1987), p. 62.

3) M. Oki, *Stereochem.*, **14**, 1 (1983).

4) S. Kohmoto, I. Koyano, T. Funabashi, K. Kishikawa, M. Yamamoto, and K. Yamada, *Tetrahedron Lett.*, **36**, 553 (1995).

5) S. Kohmoto, T. Kawatsuji, K. Ogata, M. Yamamoto, and K. Yamada, *J. Am. Chem. Soc.*, **113**, 5476 (1991).

6) S. Kohmoto, T. Funabashi, N. Nakayama, T. Nishio, I. Iida, K. Kishikawa, M. Yamamoto, and K. Yamada, *J. Org. Chem.*, **58**, 4764 (1993).

7) a) G. E. Hall and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2203 (1971); b) K. Takeuchi, T. Kitagawa, T. Toyama, and K. Okamoto, *J. Chem. Soc., Chem. Commun.*, **1982**, 313; c) K. Takeuchi, Y. Senzaki, and K. Okamoto, *J. Chem. Soc., Chem. Commun.*, **1984**, 111; d) J. Daub, H.-D. Ludemann, M. Michna, and R. M. Strobl, *Chem. Ber.*, **118**, 620 (1985).

8) a) A. Mannschreck, G. Rissmann, F. Vögtle and D. Wild, *Chem. Ber.*, **100**, 335 (1967); b) I. C. Calder and P. J. Garratt, *J. Chem. Soc. B.*, **1967**, 660.

9) a) P. J. Battye and D. W. Jones, *J. Chem. Soc., Chem. Commun.*, **1986**, 1807; b) P. J. Battye, D. W. Jones, and H. P. Tucker, *J. Chem. Soc., Chem. Commun.*, **1988**, 495.