Stereospecific Thermal Isomerization of 2,2-Dimethylbenzocyclobutenols to 2-Isopropenylphenyl Alcohols

Katsumi Iida, Masaichi Saito, and Michikazu Yoshioka*

Department of Chemistry, Faculty of Science, Saitama University, Shimo-okubo, Urawa, Saitama 338-8570, Japan

yoshioka@chem.saitama-u.ac.jp

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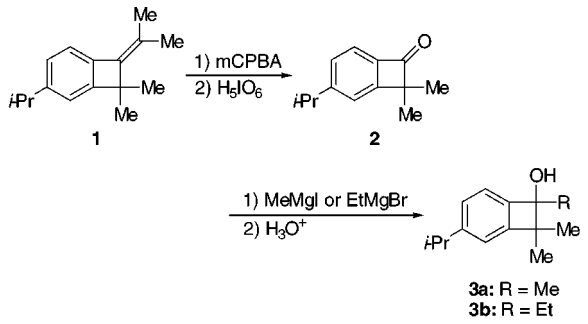
Thermolysis of the 1-alkyl-2,2-dimethylbenzocyclobutenol **3** at 160 °C gave the 2-isopropenylphenyl alcohol **8** through an (*E*)-dienol intermediate by a 1,5-sigmatropic hydrogen shift from the isopropylidene methyl group to the carbon bearing hydroxy group. In the thermolysis of each of the diastereomeric 2,2-dimethylbenzocyclobutenols **6** and **7** which have a hydroxy group on the β-carbon of the quaternary C_1-alkyl substituent, the isomerization to the 2-isopropenylphenyl alcohols **10** and **11** took place stereospecifically through a twisted (*E*)-dienol intermediate. The configuration of the newly formed chiral center in **10** and **11** was the same as that of the ring carbon bearing hydroxy group in the starting **6** and **7**.

Introduction

o-Xylylenes and its derivatives have been used extensively as synthetic intermediates in organic synthesis.[1] The physical properties and structures of these species have also been studied both theoretically and experimentally.[2] McCullough reported that the flash photolysis of 1,1-dimethyl-2-indanone and 1,1,3,3-tetramethyl-2-indanone showed transient absorption maxima at 360 and 350 nm that were assigned as 7,7-dimethyl-*o*-xylylene and 7,7,8,8-tetramethyl-*o*-xylylene, respectively.[3] The absorption spectrum of *o*-xylylene itself has λ_{max} at 373 nm.[4] The absorptions of 7,7-dimethyl-*o*-xylylene and 7,7,8,8-tetramethyl-*o*-xylylene at shorter wavelength than that of the parent *o*-xylylene are explained that the former are nonplanar and must be twisted about the "essential" single bonds.[3,5]

o-Xylylenes are also generated by thermal ring opening of benzocyclobutenes.[6] Benzocyclobutenols are known to undergo selective outward rotation of the OH group to give (*E*)-*o*-xylylenols, also named (*E*)-dienols.[7] The (*E*)-dienols generated from 2,2-dimethylbenzocyclobutenols having a bulky C_1-alkyl group are expected to have a twisted nonplanar structure because of the steric repulsion between the bulky C_7-alkyl group and a C_8-methyl group oriented inside. To characterize the nature of the (*E*)-dienol generated from 2,2-dimethylbenzocyclobutenols, we have studied the thermal reaction of 2,2-dimethylbenzocyclobutenols **3** and diastereomeric 2,2-dimethylbenzocyclobutenols **6** and **7**. We report here the stereospecific thermal isomerization of **6** and **7** to 2-isopropenylphenyl alcohols **10** and **11**, respectively, by a 1,5-sigmatropic hydrogen shift in an initially generated nonplanar (*E*)-dienol intermediate.

Scheme 1



Results and Discussion

Preparation of 2,2-Dimethylbenzocyclobutenols. The 2,2-dimethylbenzocyclobutenols **3a** and **3b** were prepared from the isopropylidenebenzocyclobutene **1**.[8] Epoxidation of **1** with *m*-CPBA followed by oxidative cleavage of the resulting epoxide with periodic acid gave the 2,2-dimethylbenzocyclobutenone **2**.[9] The reaction of **2** with methylmagnesium iodide and ethylmagnesium bromide gave **3a** and **3b**, respectively (Scheme 1).[10] The 2,2-dimethylbenzocyclobutenols **3c**, **6a**−**e**, and **7a**−**e** were prepared by the photochemical cyclization of the corresponding 2-isopropylphenyl ketones **4** and **5** (Schemes 2 and 3). The configuration of **7a** was determined by X-ray crystallographic analysis to be (1′*R**,3*S**).[8] The configurations of other 2,2-dimethylbenzocyclobutenols

(1) (a) Oppolzer, W. *Synthesis* **1978**, 793. (b) Quinkert, G.; Stark, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 637. (c) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873. (d) Segura, J. O.; Martín, N. *Chem. Rev.* **1999**, *99*, 3199.

(2) (a) Migirdicyan, E. Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400. (b) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840. (c) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820.

(3) de Fonseka, K. K.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3277.

(4) (a) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1973**, *95*, 5802. (b) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.

(5) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270.

(6) Jefford, C. W.; Bernardinelli, G.; Wang, Y.; Spellmeyer, D. C.; Buda, A.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1157.

(7) (a) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 409. (b) Iida, K.; Komada, K.; Saito, M.; Yoshioka, M. *J. Org. Chem.* **1999**, *64*, 7407.

(8) Yoshioka, M.; Iida, K.; Kawata, E.; Maeda, K.; Kumakura, S.; Hasegawa, T. *J. Org. Chem.* **1997**, *62*, 2655.

(9) Nagarkatti, J. P.; Ashley, K. R. *Tetrahedron Lett.* **1973**, 4599.

(10) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 415.

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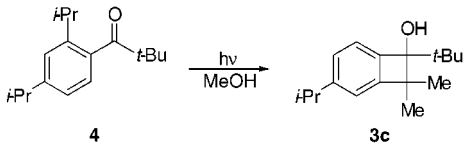
Scheme 2



4 3c

Scheme 3

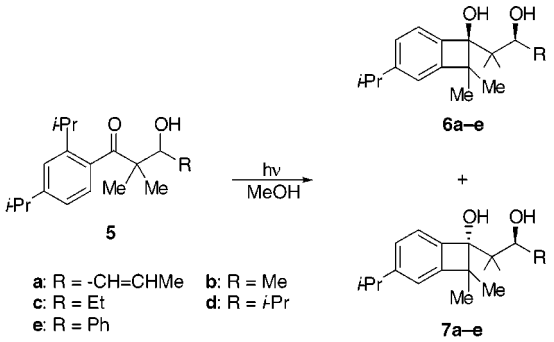


Table 1. Thermal Isomerization of 2,2-Dimethylbenzocyclobutenols 3[a]

	product ratio[b]	
compd	**8**	**9**
3a	33	67
3b	38	62
3c	100	

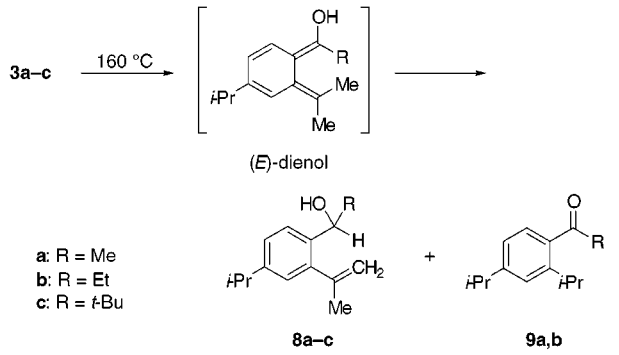
[a] Heated at 160 °C in a sealed glass tube. After 4 h, the starting benzocyclobutenols completely disappeared and only **8** and **9** were produced. [b] Determined by ^{1}H NMR spectroscopy directly in the reaction mixture.

6 and **7** were deduced by comparison of their chromatographic behavior with those of **6a** and **7a**.[8]

Thermal Reaction of 1-Alkyl-2,2-dimethylbenzocyclobutenols. When 1-methyl (**3a**) and 1-ethyl (**3b**) substituted 2,2-dimethylbenzocyclobutenols were heated at 160 °C for 4 h in a glass tube, they were converted into the 2-isopropenylphenyl alcohol **8a**,**b** and the 2-isopropylphenyl ketone **9a,b** in a ratio given in Table 1. However, when the 1-*tert*-butyl-2,2-dimethylbenzocyclobutenol **3c** was heated under the same conditions, it was converted quantitatively into the (2′-isopropenylphenyl)-2,2-dimethylpropanol **8c** (Scheme 4).

We have recently reported that 1-methylbenzocyclobutenol undergoes selective opening to the (*E*)-dienol and that the resulting (*E*)-dienol undergoes isomerization to 2-methylacetophenone by two processes, viz. intramolecular 1,5-sigmatropic hydrogen shift from the methyl group and intermolecular proton transfers.[7b] The 2-isopropylphenyl ketones **9a** and **9b** would arise through the (*E*)-dienol by a hydrogen shift from the alkyl group on the carbon bearing OH group and/or by intermolecular process. However, the thermolysis of **3c** did not give the corresponding ketone. The (*E*)-dienol formed from **3c** has no hydrogen to undergo 1,5-sigmatropic shift to give the ketone, and the (*Z*)-dienol isomerizes rapidly to the ketone by a 1,5-sigmatropic hydrogen shift from the OH group.[11] We have recently reported that heating 2-(1′-hydroxy-1′,2′-dihydrobenzocyclobuten-1′-yl)-2,4-dimethylpentan-3-ol without solvent at 150 °C gave only isobutyrophenone by selective opening to the (*E*)-dienol. The

Scheme 4



resulting (*E*)-dienol was converted by intermolecular proton transfers into 1-(*o*-methylphenyl)-3-hydroxy-2,2,4-trimethylpentan-1-one which further underwent retroaldol cleavage to give isobutyrophenone.[13] Therefore, no formation of the ketone from **3c** indicates that **3c** selectively opens to the (*E*)-dienol and that the resulting (*E*)-dienol undergoes 1,5-sigmatropic hydrogen shift from the isopropylidene methyl group to the carbon bearing the OH group to give **8c** much faster than intermolecular proton transfers to give the ketone. The 7,7-dimethyl-*o*-xylylenes are known to undergo a fairly rapid 1,5-sigmatropic hydrogen shift to give *o*-alkyl-α-methylstyrenes.[12] Thus, the 2-isopropenylphenyl alcohols **8a**−**c** would arise from the initially formed (*E*)-dienol by a hydrogen shift from the isopropylidene methyl group.

Stereospecific Thermal Isomerization of Diastereomeric 2,2-Dimethylbenzocyclobutenols to 2-Isopropenylphenyl Alcohols. As mentioned above, the thermolysis of 1-*tert*-butyl-2,2-dimethylbenzocyclobutenol **3c** gave only the isopropenylphenyl alcohol **8c** through the (*E*)-dienol intermediate. McCullough suggested that the thermal isomerization of 1,1,3,3-tetramethyl-2-indanone to *o*-isopropyl-α-methylstyrene occurred via a nonplanar *o*-xylylene.[3] To obtain information for the geometry of the (*E*)-dienol generated from the 2,2-dimethylbenzocyclobutenol having a bulky C_1-substituent and to examine the process of a hydrogen shift in the (*E*)-dienol, the thermolysis of diastereomeric 2,2-dimethylbenzocyclobutenols **6a**−**e** and **7a**−**e** was investigated. Heating 2-(1′-hydroxy-2′,2′-dimethylbenzocyclobuten-1′-yl)-2-methylhex-4-en-3-ol (**6a**) at 160 °C for 4 h in a glass tube gave 1-(2′-isopropenylphenyl)-2,2-dimethylhex-4-ene-1,3-diol (**10a**) in 84% yield. Heating the diastereomeric 2,2-dimethylbenzocyclobutenol **7a** under the same conditions gave the 1,3-diol **11a** in 84% yield (Scheme 5). The configurations of **10a** and **11a** were established by NOE experiments. The 1,3-diols **10a** and **11a** reacted with phenylboronic acid to give cyclic esters **12** and **13**, respectively. In the phenylboronic ester **13**, the definite enhancement (8%) of the signal (δ 5.44) for a ring hydrogen adjacent to the double bond was observed on irradiation of a ring hydrogen (δ 4.43) adjacent to the aromatic ring. No similar enhancement was observed in the phenylboronic ester **12** (Scheme 5). Therefore, the configurations of **10a** and **11a** must be (1*S**,3*S**) and (1*R**,3*S**), respectively. Thus, each of the asymmetric

(11) Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.

(12) (a) Starr, J. E.; Eastman, R. H. *J. Org. Chem.* **1966**, *31*, 1393. (b) Korth, H.-G.; Sustmann, R.; Lommes, P.; Paul, T.; Ernst, A.; de Groot, H.; Hughes, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1994**, *116*, 2767.

(13) Kawata, E.; Saito, M.; Yoshioka, M. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1015.

Scheme 5

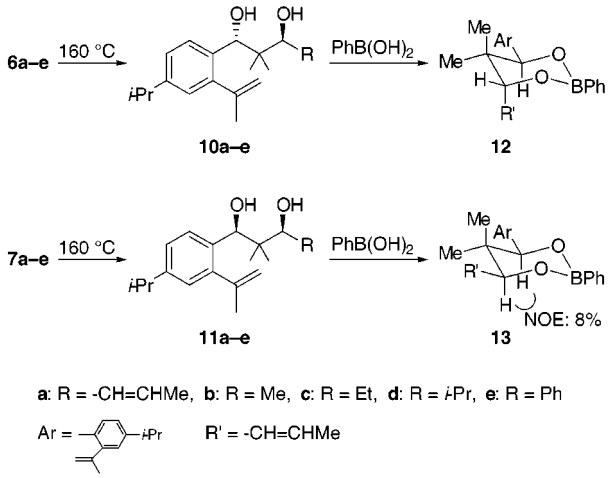


Table 2. Stereospecific Thermal Isomerization of 6 and 7[a]

	yield (%)[b]	
compd	**10**	**11**
6a	84	
6b	71	
6c	71	
6d	82	
6e	63	
7a		84
7b		67
7c		71
7d		82
7e		63

[a] Heated at 160 °C for 4 h. [b] Isolated yield.

carbons in the isomerization products has the same configuration as that in the starting 2,2-dimethylbenzocyclobutenols. The 2,2-dimethylbenzocyclobutenols **6b**−**e** and **7b**−**e** also underwent stereospecific isomerization to **10b**−**e** and **11b**−**e**, respectively, under the same conditions. The results of the thermolysis of the diastereomeric benzocyclobutenols **6** and **7** are given in Table 2.

In the thermolysis of **6** and **7**, neither the ketol **5** nor the isobutyrophenone **4** (retro-aldol cleavage product of **5**) was detected by the ^{1}H NMR analysis of the reaction mixture, suggesting that even the 2,2-dimethylbenzocyclobutenols **6** and **7**, which have a bulky C_1-substituent, underwent selective opening to the (*E*)-dienol[13] and that the resulting (*E*)-dienol underwent rapid isomerization to diol **10** or **11**. The (*Z*)-dienol undergoes a rapid 1,5-sigmatropic hydrogen shift from the OH group to give the ketone.[11] The stereospecific isomerization of **6** and **7** to **10** and **11** may be attributed to a nonplanar geometry of the (*E*)-dienol intermediate. To examine the steric effects affecting the geometry of the (*E*)-dienol, ab initio calculations were carried out on (*E*)-dienols **14**−**16** by employing a HF method with a 6-31G* basis set. Even the (*E*)-dienol **14** is nonplanar. The dihedral angle between C_1−C_7 and C_6−C_8 becomes markedly larger with bulkier substituents on C_7 and C_8. The (*E*)-dienol **16** has a dihedral angle between C_1−C_7 and C_6−C_8 of 71.7° (Table 3), suggesting that the (*E*)-dienols from **3c**, **6a**−**e**, and **7a**−**e** have a highly twisted structure. The geometry of the (*E*)-dienols formed from these 2,2-dimethylbenzocyclobutenols must be **A** or **B** as depicted in Scheme 6 so that the interaction between the C_7-quaternary alkyl and C_8-methyl groups is minimum

Scheme 6

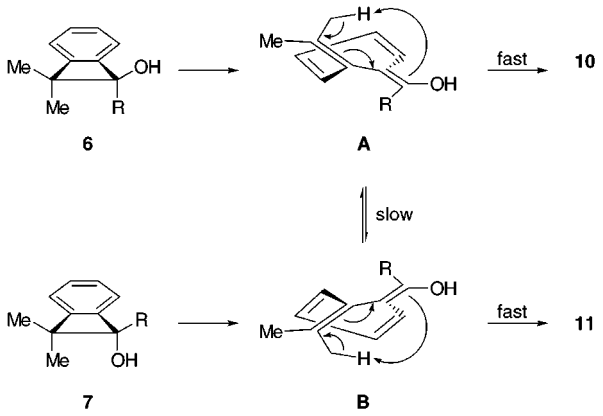
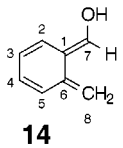
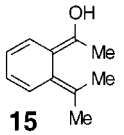
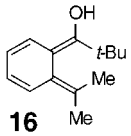


Table 3. Selected Torsion Angles (deg) of (*E*)-Dienols 14−16 Calculated by HF/6-31G*

structure	C_7–C_1–C_6–C_8	C_2–C_3–C_4–C_5
 **14**	25.8	5.6
 **15**	56.0	14.4
 **16**	71.7	18.0

during conformational change after ring opening. It has been reported that *o*-xylylenes having two methyl groups on an exo-methylene carbon were nonplanar and isomerized fairly rapid to α-methylstyrenes by a symmetry-forbidden antrafacial 1,5-sigmatropic hydrogen shift.[3,5,12] The geometry of the (*E*)-dienols formed from **6** and **7** is suitable for an antrafacial 1,5-sigmatropic hydrogen shift to give **10** or **11**, a newly formed chiral center in which has the same configuration as that of the ring carbon bearing hydroxy group in the starting 2,2-dimethylbenzocyclobutenols **6** and **7**. The interconversion between **A** and **B** is probably slow because of the steric interaction between the C_7-quaternary alkyl and C_8-methyl groups. The hydrogen migration from the C_8-methyl group to C_7 would occur before ring inversion and on one side of the C_7-containing plane, reflecting the stereospecific isomerization of the diastereomeric 2,2-dimethylbenzocyclobutenols **6** and **7** to the 2-isopropenylphenyl alcohols **10** and **11**, respectively.

In conclusion, the 2,2-dimethylbenzocyclobutenol underwent thermal opening to the (*E*)-dienol and the resulting (*E*)-dienol isomerized to the 2-isopropenylphenyl alcohol by a 1,5-sigmatropic hydrogen shift from the isopropylidene methyl group to the carbon bearing OH group. The (*E*)-dienols formed from 2,2-dimethylbenzocyclobutenols having a bulky C_1-alkyl substituent had a twisted geometry and underwent stereospecific hydrogen migration before ring flip.

Experimental Section

Melting points were uncorrected and boiling points were measured from the oven temperatures in Kugelrohr distillation. ^{1}H NMR spectra were recorded at 200 or 400 MHz using tetramethylsilane as an internal standard with $CDCl_3$ as a solvent. ^{13}C NMR spectra were recorded at 50 or 100 MHz with $CDCl_3$ as a solvent. IR spectra were recorded for solutions in CCl_4 unless otherwise stated. Methods for the preparation of the diastereomeric 2,2-dimethylbenzocyclobutenols **6a**−**e** and **7a**−**e** and their physical properties have already been described in a previous paper.[8]

Preparation of 4-Isopropyl-2,2-dimethylbenzocyclobuten-1(2H)-one (2). To a solution of 1-isopropylidene-4-isopropyl-2,2-dimethyl-1,2-dihydrobenzocyclobutene (**1**)[8] (360 mg 1.68 mmol) in CH_2Cl_2 (20 mL) was added a solution of *m*-CPBA (337 mg (1.95 mmol) in CH_2Cl_2 (10 mL) at room temperature. After 30 min of stirring at room temperature, a solution of periodic acid (350 mg, 1.53 mmol) in THF (10 mL) was added. After 10 min of stirring at room temperature, the mixture was treated successively with saturated solutions of $NaHCO_3$, $Na_2S_2O_3$, and NaCl and extracted with CH_2Cl_2. After the solvent was removed, the residue was subjected to chromatography on silica gel (hexane:ethyl acetate = 8:1) to give the 2,2-dimethylbenzocyclobutenone (**2**) (257 mg, 80%) as an oil: IR 1780 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.29 (6H, d, J = 7 Hz), 1.45 (6H, s), 2.98 (1 H, sept, J = 7 Hz), 7.2−7.4 (3H, m); ^{13}C NMR (50 MHz) δ 22.8 (2q), 23.8 (2q), 35.3 (d), 64.5 (s), 119.0 (d), 121.6 (d), 128.3 (d), 142.1 (s), 157.6 (s), 163.2 (s), 196.3 (s).

Preparation of 2,2-Dimethylbenzocyclobutenols 3a and 3b. To 50 mg (2.1 mmol) of magnesium in dry ether (5 mL) was added slowly at 0 °C 2.2 mmol of MeI or EtBr in dry ether (5 mL). After the magnesium dissolved completely, 257 mg (1.36 mmol) of 2,2-dimethylbenzocyclobutenone (**2**) in dry ether (1 mL) was added at 0 °C. After overnight stirring, the mixture was treated with a saturated NH_4Cl solution and extracted with ether. After the solvent was removed, the residue was subjected to chromatograpy on silica gel (hexane: ethyl acetate = 25:1) to give 2,2-dimethylbenzocyclobutenols **3a** and **3b**.

4-Isopropyl-1,2,2-trimethyl-1,2-dihydrobenzocyclobuten-1-ol (3a): mp 70−71 °C (from hexane); IR ($CHCl_3$) 3600 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.23 (6H, d, J = 7 Hz), 1.32 (3H, s), 1.33 (3H, s), 1.51 (3H, s), 2.18 (1H, s), 2.88 (1H, sept, J = 7 Hz), 7.0−7.2 (3H, m); ^{13}C NMR (100 MHz) δ 22.1 (q), 23.0 (q), 23.8 (q), 24.2 (q), 24.3 (q), 34.9 (d), 53.0 (s), 81.1 (s), 118.8 (d), 120.9 (d), 126.0 (d), 146.1 (s), 150.4 (s), 152.1 (s). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.96; H, 9.89.

Preparation of 1-*tert*-Butyl-4-isopropyl-2,2-dimethyl-1,2-dihydrobenzocyclobuten-1-ol (3c). A solution of 2,4-diisopropylpivalophenone (**4**) (600 mg) in methanol (120 mL) was irradiated with a high-pressure mercury lamp through a Pyrex filter under argon for 24 h. After the solvent was removed under reduced pressure, the residue was subjected to chromatograpy on silica gel (hexane:ethyl acetate = 6:1) to give the 2,2-dimethylbenzocyclobutenol **3c** as an oil: ^{1}H NMR (400 MHz) δ 1.11 (9H, s), 1.24 (6H, d, J = 7 Hz), 1.36 (3H, s), 1.59 (3H, s), 2.13 (1H, s), 2.88 (1H, sept, J = 7 Hz), 6.9−7.2 (3H, m); ^{13}C NMR (100 MHz) δ 24.2 (q), 24.3 (q), 24.9 (q), 27.0 (q), 27.7 (q), 34.8 (d), 37.9 (s), 54.8 (s), 89.1 (s), 117.8 (d), 121.9 (d), 125.6 (d), 144.0 (s), 150.2 (s), 153.2 (s).

Thermolysis of 2,2-Dimethylbenzocyclobutenols 3. 2,2-Dimethylbenzocyclobutenols **3** (30 mg) were placed in an 8-mm diameter Pyrex tube under reduced pressure. The tube was heated at 160 °C for 4 h. The ^{1}H NMR spectrum of the reaction mixture showed the complete disappearance of the starting 2,2-dimethylbenzocyclobutenol **3** and the clean formation of the 2-isopropenylphenyl alcohol **8** and the ketone **9**. The compounds **8** and **9** were isolated by silica gel column chromatography using hexane and ethyl acetate (4:1) as an eluent.

1-(2′-Isopropenyl-4′-isopropylphenyl)-2,2-dimethylpropanol (8c): bp 150−152 °C at 0.6 mmHg; IR 3610 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.93 (9H, s), 1.24 (6H, d, J = 7 Hz), 1.69 (1H, br s), 2.06 (3H, d, J = 1 Hz), 2.87 (1H, sept, J = 7 Hz), 4.77 (1H, s), 4.86 (1H, d, J = 1 Hz), 5.20 (1H, quint, J = 1 Hz), 6.95 (1H, s), 7.17 (1H, d, J = 8 Hz), 7.47 (1H, d, J = 8 Hz); ^{13}C NMR (100 MHz) δ 23.9 (2q), 25.6 (q), 26.4 (3q), 33.7 (d), 36.4 (s), 77.2 (d), 115.9 (t), 124.6 (d), 126.1 (d), 127.4 (d), 136.4 (s), 143.9 (s), 145.8 (s), 147.6 (s). Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.64; H, 10.73.

Thermolysis of Diastereomeric Benzocyclobutenols 6 and 7. Each of the diastereomeric 2,2-dimethylbenzocyclobutenols (100 mg) **6** and **7** was placed in an 8-mm diameter Pyrex tube under reduced pressure. The tube was heated at 160 °C for 4 h. The mixture was subjected to chromatography on silica gel (hexane:ethyl acetate = 4:1 to 8:1) to give the 2-isopropenylphenyl alcohol **10** or **11**. The ^{1}H NMR spectra of each of the reaction mixtures before chromatography revealed that **6** and **7** isomerized cleanly to **10** and **11**, respectively.

(1*S,3*S**)-1-(2′-Isopropenyl-4′-isopropylphenyl)-2,2-dimethylhex-4-ene-1,3-diol (10a):** bp 127−128 °C at 0.5 mmHg; IR 3320 (br), 3610 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.77 (3H, s), 0.86 (3H, s), 1.24 (6H, d, J = 7 Hz), 1.71 (3H, d, J = 6 Hz), 2.04 (3H, s), 2.87 (1H, sept, J = 7 Hz), 3.40−3.70 (2H, br s), 4.00 (1H, d, J = 5 Hz), 4.85 (1H, s), 5.10 (1H, s), 5.16 (1H, s), 5.50−5.80 (2H, m), 6.92 (1H, d, J = 2 Hz), 7.13 (1H, dd, J = 2 and 8 Hz), 7.54 (1H, d, J = 8 Hz); ^{13}C NMR (50 MHz) δ 17.7 (q), 21.0 (q), 21.7 (q), 23.9 (2q), 25.4 (q), 33.6 (d), 41.6 (s), 75.7 (d), 80.1 (d), 115.8 (t), 124.7 (d), 126.0 (d), 128.1 (d), 128.3 (d), 130.5 (d), 135.4 (s), 143.6 (s), 145.8 (s), 147.6 (s). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.65; H, 10.09.

(1*R,3*S**)-1-(2′-Isopropenyl-4′-isopropylphenyl)-2,2-dimethylhex-4-ene-1,3-diol (11a):** mp 87−88 °C (from pentane); ^{1}H NMR (200 MHz) δ 0.44 (3H, s), 1.01 (3H, s), 1.24 (6H, d, J = 7 Hz), 1.70 (3H, d, J = 6 Hz), 2.06 (3H, s), 2.86 (1H, sept, J = 7 Hz), 3.30−3.80 (2H, br s), 4.05 (1H, d, J = 7 Hz), 4.86 (1H, s), 5.05 (1H, s), 5.19 (1H, s), 5.45−5.80 (2H, m), 6.91 (1H, d, J = 2 Hz), 7.12 (1H, dd, J = 2 and 8 Hz), 7.48 (1H, d, J = 8 Hz); ^{13}C NMR (50 MHz) δ 13.4 (q), 17.7 (q), 22.8 (q), 23.9 (2q), 25.5 (q), 33.6 (d), 42.1 (s), 78.1 (d), 83.1 (d), 115.9 (t), 124.6 (d), 125.9 (d), 128.0 (d), 128.7 (d), 130.4 (d), 135.5 (s), 143.6 (s), 146.0 (s), 147.6 (s). Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.38; H, 10.02.

Reaction of 1,3-Diols 10a and 11a with Phenylboronic Acid. A solution of each of the 1,3-diols **10a** and **11a** (18 mg, 0.06 mmol) and phenylboronic acid (8 mg, 0.065 mmol) in benzene (2 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to afford the boronic ester **12** (22 mg) or **13** (21 mg). For **12**: an oil; ^{1}H NMR (400 MHz) δ 0.85 (3H, s), 0.87 (3H, s), 1.25 (6H, d, J = 7 Hz), 1.77 (3H, d, J = 6 Hz), 2.10 (3H, s), 2.88 (1H, sept, J = 7 Hz), 4.32 (1H, d, J = 6 Hz), 4.95 (1H, s), 5.24 (1H, s), 5.38 (1H, s), 5.64 (1H, dd, J = 6 and 15 Hz), 5.78 (1H, dq, J = 6 and 15 Hz), 6.9−8.0 (8H, m). For **13**: an oil; ^{1}H NMR (400 MHz) δ 0.70 (3H, s), 0.81 (3H, s), 1.27 (6H, d, J = 7 Hz), 1.79 (3H, d, J = 7 Hz), 2.10 (3H, s), 2.90 (1H, sept, J = 7 Hz), 4.43 (1H, d, J = 7 Hz), 4.96 (1H, s), 5.24 (1H, s), 5.44 (1H, s), 5.55 (1H, dd, J = 7 and 15 Hz), 5.88 (1H, dq, J = 7 and 15 Hz), 6.9−8.3 (8 H, m). Irradiation of the signal at δ 5.44 led to NOE enhancement of the signal at δ 4.43.

Supporting Information Available: Physical properties of compounds **3b**, **8a**,**b**, **10b**−**e**, and **11b**−**e** and ^{1}H and ^{13}C NMR spectra for compounds **2**, **3c**, **8a**, **10e**, **11e**, **12**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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