Radical-Cation-Initiated Diels-Alder Di- and Trimerization of 3,4-Dimethoxypropenylbenzene: Stereochemical Correlation with the Lignans Galbulin and Isogalbulin

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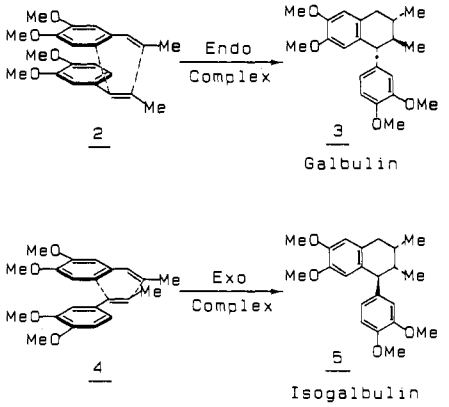
Abstract: Diels-Alder reactions of methylisoeugenol (3,4-dimethoxypropenylbenzene, **1**) initiated by the radical cation tris(*p*-bromophenyl)aminium hexachloroantimonate (BAHA) lead to the naphthalene regioisomers **7** and **8** as well as the trimers **9-15**. The radical-cation origins of these products have been established through detailed regio- and stereochemical studies which indicate that the initial Diels-Alder step proceeds with (1) a lack of regiospecificity and (2) a preference for the endo rather than the exo reaction configuration. The number of regio- and stereoisomers is substantially reduced in the BAHA-initiated rearrangement of the cyclobutane **16**, which affords only the naphthalene **7** and the trimers **11-13**. While the initial Diels-Alder step provides the same stereochemistry that is found in the lignans galbulin (**3**) and isogalbulin (**5**), the formation of the regioproducts (**8**, **14**, and **15**) and the involvement of a third unit of **1** to form the trimers (**9-15**) preclude any straightforward correlation of radical-cation Diels-Alder reactions with the biosynthesis of the aryltetralin lignans.

Recent, elegant studies[1] of the role of radical cations in pericyclic reactions have focused attention upon these reactive intermediates and their synthetic potential in the formation of complex ring systems. However, with the exception of Kikuchi's synthesis of the neolignan magnoshinin,[2] there has been no explicit study of the role that radical-cation chemistry might play in the formation of lignans from their biogenetic precursors. We have been intrigued by the possibility that radical-cation Diels-Alder reactions of methylisoeugenol (3,4-dimethoxypropenylbenzene, **1**) might lead to lignans of the aryltetralin class with stereochemistry determined by the transition state of the Diels-Alder reaction, as shown in Scheme I. Thus, if *trans*-**1** were to undergo a Diels-Alder dimerization via an endo complex (**2**), the stereochemistry corresponding to the lignan galbulin (**3**)[3] should result. In contrast, dimerization through the exo complex (**4**) should lead to stereochemistry corresponding to that of the lignan isogalbulin (**5**).[4] In order to evaluate this strategy for the formation of aryltetralins, we have examined the radical-cation chemistry of **1** and report the results of these studies below.

Radical-Cation Chemistry. Treatment of *trans*-**1**[5] with tris(*p*-bromophenyl)aminium hexachloroantimonate (BAHA) leads to rapid formation of the well-known acid-catalyzed dimer **6**[6] (86%). However, in the presence of a nonoxidizable base such as Na_2CO_3, the yield of **6** is greatly diminished, and a complex mixture of radical-cation-initiated di- and trimerization products results (Scheme II).[7] Extensive preparative HPLC work has led to the isolation in pure form of all products produced in this reaction in >1%: the acid-catalyzed dimer **6**, the naphthalenes **7** and **8**, and the trimers **9-15**.

The regio- and stereochemical correlation of these products was greatly facilitated by a study of the radical-cation chemistry of the cyclobutane **16** (Scheme III). Cyclobutane **16** is available through the photodimerization of **1** in neat or very concentrated solutions. This sluggish photoreaction apparently originates from a short-lived singlet intermediate, as the formation of **16** is greatly diminished by dilution and does not occur at all in moderately dilute solution. That **16** has the cis-anti-cis stereochemistry shown in Scheme III was readily established by a comparison of its NMR spectrum with that of the known *cis-anti-cis*-cyclobutane derived from the photodimerization of *trans*-anethole.[8] The cyclobutane protons in **16** occur at δ 3.43 and 2.80 and those of the *trans*-anethole dimer at δ 3.45 and 2.85.

Scheme I



Treatment of **16** with BAHA as indicated in Scheme III leads to partial reversion to methylisoeugenol (**1**). This liberated methylisoeugenol apparently then serves to trap the rearranged cyclobutane radical cation to form the trimers **11-13**. In addition,

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(1) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A., Jr.; Reynolds, D. W.; Wirth, D. D.; Chiou, H.-S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371, and references therein.

(2) Kadota, S.; Tsubono, K.; Makino, K.; Takeshita, M.; Kikuchi, T. *Tetrahedron Lett.* **1987**, *28*, 2857.

(3) Carnmalm, B. *Acta Chem. Scand.* **1954**, 1827.

(4) Birch, A. J.; Milligan, B.; Smith, E.; Speake, R. N. *J. Chem. Soc.* **1958**, 4471.

(5) Methylisoeugenol as obtained from Aldrich Chemical Co. was a trans:cis mixture (93:7). Pure *trans*-methylisoeugenol (**1**) was isolated by preparative GLC for this work.

(6) (a) MacMillan, J.; Martin, I. L.; Morris, D. J. *Tetrahedron* **1969**, *25*, 905. See also: (b) Clark-Lewis, J. W.; Nair, V. *Aust. J. Chem.* **1967**, *20*, 2137. (c) von E. Doering, W.; Berson, J. A. *J. Am. Chem. Soc.* **1950**, *72*, 1118. (d) Haworth, R. D.; Mavin C. R. *J. Chem. Soc.* **1931**, 1363. (e) Muller, A.; Toldy, L.; Halmi, G.; Meszaros, M. *J. Org. Chem.* **1951**, *16*, 481.

(7) Di-*tert*-butylpyridine has been used commonly to suppress acid-catalyzed reactions in radical-cation systems: Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7933. Sodium carbonate is also quite effective for this purpose and has been used throughout this work so that earlier results (Shepherd, T. A. M.S. Thesis, University of Cincinnati, 1983) could be compared with later studies.

(8) Nozaki, H.; Otani, I.; Noyori, R.; Kawanisi, M. *Tetrahedron* **1968**, *24*, 2183.

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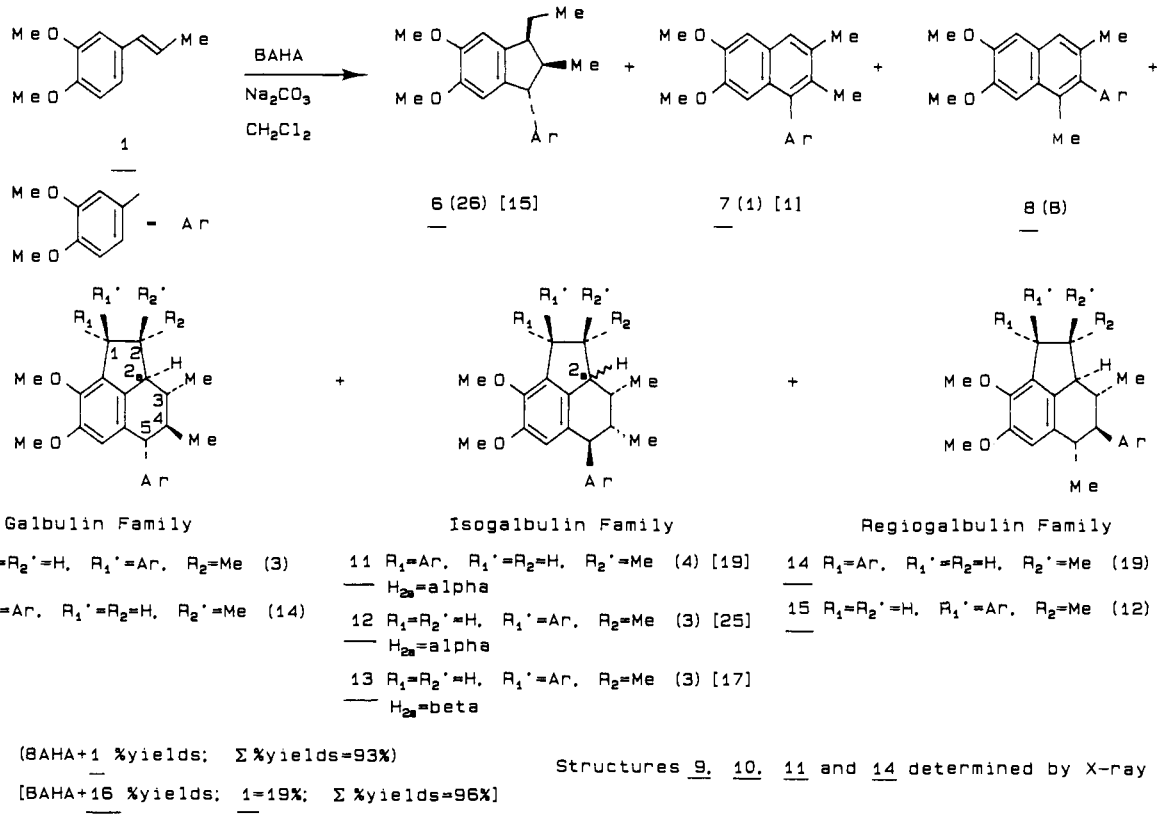
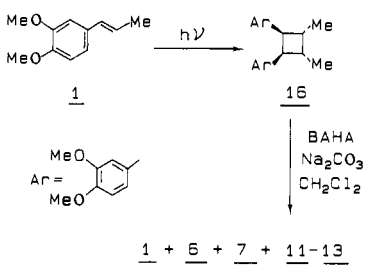
Scheme II



Scheme III



the acid-catalyzed dimer **6** and the naphthalene **7** are produced as well.

In Scheme II, the yields from the methylisoeugenol reaction are displayed in parentheses and those from the reaction of cyclobutane **16** in brackets. Even though both of these reactions are quite complex, the mass balances are in excess of 90% in both cases. Finally, in order to facilitate subsequent discussion of this stereochemically complex array of trimers, the trimers have been grouped into three families: the galbulin family, which has the galbulin regio- and stereochemistry in the saturated six-membered ring (*trans*-3,4-dimethyl groups); the isogalbulin family, which has the isogalbulin regio- and stereochemistry at these same positions (*cis*-3,4-dimethyl groups); the regiogalbulin family, which has all-trans stereochemistry in the saturated six-membered ring, but an inverted regiochemistry in the 4- and 5-positions.

Structural Assignments. The assignment of structure to the naphthalene regioisomers **7** and **8** is based upon the fact that **7** is related to the known oxidation product of isoeugenol[9] and is the only naphthalene produced in the oxidative rearrangement of the cyclobutane **16**. Therefore, the naphthalene **8** must arise from the oxidation of a precursor to the regiogalbulin family of trimers.

In the initial phase of this structural study, a complete 300-MHz NMR decoupling study was conducted with each of the trimers

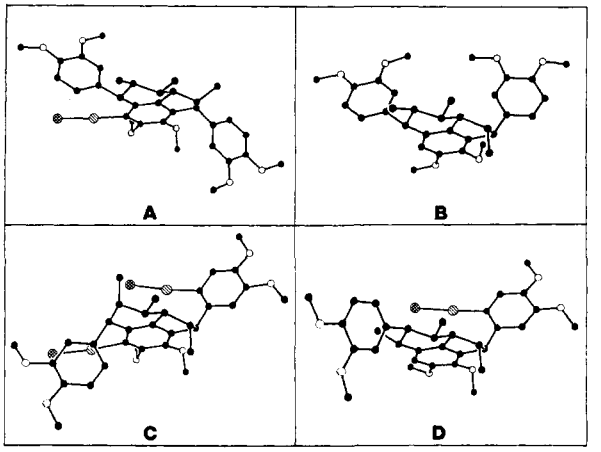


Figure 1. X-ray crystal structures for (A) a monomercurated derivative of **9**, (B) **10**, (C) a dimercurated derivative of **11**, and (D) a monomercurated derivative of **14**: carbon, ●; oxygen, O; bromine, ⊗; mercury, ⊗.

9–15. On the basis of these results at least one member of each of the three trimer families was selected for an X-ray crystallographic structure determination. Four successful X-ray crystal studies were conducted, and the results of these studies are shown in Figure 1.[10] These results confirm the structures of the trimers **9–11** and **14**.

The structure assignments for the remaining three trimers, **12**, **13**, and **15**, are based upon chemical correlation with the *cis*-dimethylcyclobutane **16**, ^{1}H NMR coupling data, and molecular modeling calculations. That **12** and **13** are members of the isogalbulin family is indicated by the observation that these two trimers are products of the cyclobutane reaction in which the *cis*-dimethyl stereochemistry of the starting cyclobutane is in-

(9) Kuo, Y. H.; Lin, S. T. *Experientia* **1983**, *39*, 991, and references therein.

(10) The X-ray crystal study of trimer **10** was conducted at Nicolet Instruments in Madison, WI, and the X-ray studies of the other trimers, **9**, **11**, and **14**, were done using the X-ray crystallographic facilities at the University of Cincinnati.

Table I. ^{1}H NMR Coupling Constants (J), Calculated Dihedral Angles (CDA),[a] and Experimentally Determined Dihedral Angles (XDA)[b] for the Trimers **9–15**

trimer positn	galbulin family			isogalbulin family			regiogalbulin family		
	J, Hz	CDA	XDA	J, Hz	CDA	XDA	J, Hz	CDA	XDA
		9			**12**			**15**	
1–2	9	154	160	9.3	135		9.3	141	
2–2a	9.6	155	160	9.9	148		9.6	151	
2a–3	9.6	178	179	10.3	177		9.6	179	
3–4	10.2	175	171	<4.0	67		10.2	175	
4–5	10.2	165	165	0.0	76		10.2	164	
		10			**11**			**14**	
1–2	0.0	98	86	0.0	98	83	0.0	101	88
2–2a	6.3	34	29	6.0	40	36	6.3	34	29
2a–3	10.8	179	168	11.7	178	166	10.8	180	167
3–4	10.5	180	178	2.7	63	62	10.8	175	176
4–5	10.5	156	164	0.0	85	88	10.2	162	170
					13				
1–2				0.0	107				
2–2a				6.0	36				
2a–3				10.5	7				
3–4				<4.0	44				
4–5				0.0	78				

[a] Dihedral angles calculated with the July 1986 CHEM-X molecular modeling package. [b] Dihedral angles calculated from X-ray crystallography data.

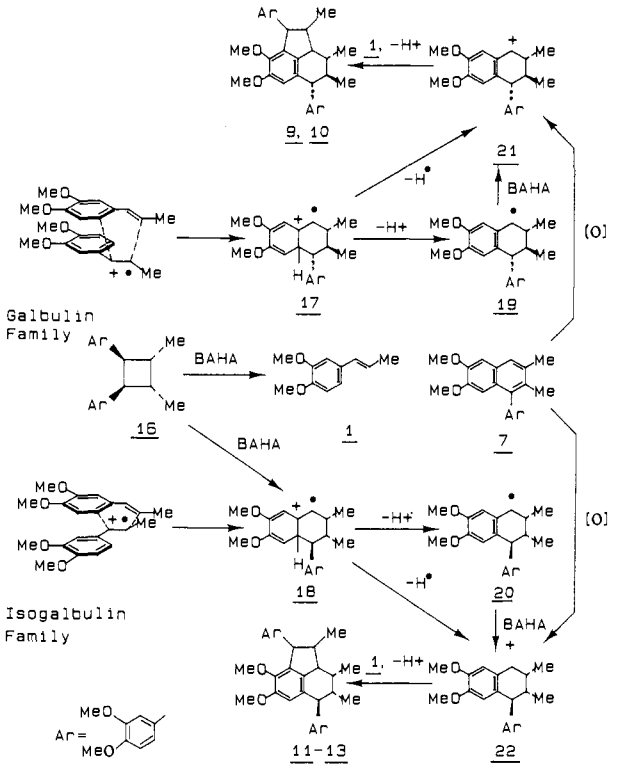
corporated into the trimers (see Scheme III). Furthermore, the coupling constants between the protons on the saturated six-membered rings of **12** and **13** ($J_{2a,3}$, $J_{3,4}$, and $J_{4,5}$) are, respectively, 10.3, <4, and ~0 Hz for **12** and 10.5, <4, and ~0 Hz for **13** (Table I). These values are consistent with the corresponding coupling constants (11.7, 2.7, and ~0 Hz) found for **11**, the structure of which has been unequivocally established by X-ray. Finally, the dihedral angles between all carbon–hydrogen bonds on saturated ring carbons have been determined by MM2 calculations and compared with those dihedral angles available from the X-ray crystallographic data (Table I). Not only are these experimental and calculated dihedral angles in reasonably good agreement, but they are consistent with the corresponding ^{1}H coupling constants.[11] Therefore, the consistency between the calculated dihedral angles and the coupling constants of those trimers for which no X-ray data are available (**12**, **13**, and **15**) is taken to be good evidence for the stereochemistries of these trimers.

Discussion

The above stereochemical studies have led to several very interesting correlations: (1) In all cases the arylpropenyl unit, which serves as the radical-cation dienophile, is incorporated with retention of configuration, a trans geometry at positions 4 and 5 (Scheme II). (2) This same unit is incorporated in either of the two possible orientations in comparable amounts, **7** + **9** + **10** + **11** + **12** + **13** = 28% and **8** + **14** + **15** = 39%. (3) There is a preference for reaction via the endo versus the exo complex (Scheme I), **9** + **10** = 17% versus **11** + **12** + **13** = 10%. These observations strongly support a concerted radical-cation Diels–Alder reaction as the initial step in the formation of these trimers (Scheme IV). Thus, it seems that all of the products listed in Scheme II, except **6**, arise via an initial radical-cation Diels–Alder reaction as outlined in Scheme IV.

While there is a marked preference for the initial Diels–Alder step to proceed through the endo complex **2**, which maximizes overlap between the donor and acceptor partners, the exo complex **4** does make a significant contribution to the trimer mixture. As a result, the more effective synthetic strategy for restricting the number of isomers is to prepare the aryltetralin skeleton via a radical-cation rearrangement of a cyclobutane such as **16** rather

Scheme IV



then via the Diels–Alder route. This cyclobutane approach allows one to fix the stereochemistries of the methyl-bearing carbon atoms and apparently also that of the aryl-bearing carbon atom. Thus, the cyclobutane **16** affords only trimers in the isogalbulin family, and of the possible isomers in this family, only those trimers **11–13** with the more stable trans geometry at positions 4 and 5 are observed. While this cyclobutane approach has been tested only with the *cis*-dimethyl isomer **16**, the galbulin family presumably could be accessed from the *trans*-dimethyl isomer of **16**.

The naphthalenes **7** and **8** must arise from the further oxidation of the initial Diels–Alder adducts. In the case of **7**, these adducts would be **17** and **18**. The precise sequence of steps leading to **7** is uncertain, but very probably proceeds through the radicals **19** and **20** and the cations **21** and **22**. These same radical or ionic species are apparently efficiently trapped by a third molecule of methylisoeugenol (**1**), and this trapping displays a strong tendency

(11) Since trimer **13** constitutes a unique member of this series of trimers in that it is the only trimer with a β-2a-hydrogen, and since there is no closely related structure for which X-ray data were available, all possible structures of the isogalbulin family were examined by MM2 calculations. The only stereochemistry found to be consistent with the observed proton coupling constants is that of **13**.

to occur from the side opposite to the methyl group that ultimately resides at position 3 in the trimers. Thus, only in trimer **13** is the stereochemical relationship between positions 2a and 3 cis.

Finally, it should be noted that in many naturally occurring aryltetralins, a hydroxyl substituent is located at the site of the radical in **19** and **20** or the carbocation in **21** and **22**. While this correlation may be coincidental, it might well be the consequence of the trapping of a radical such as **19** or **20** with molecular oxygen or a carbocation such as **21** or **22** with water. In this work, several attempts have been made to realize this type of trapping of post-Diels–Alder species. To date these efforts have all led to trapping of the radical cation of methylisoeugenol (**1**) instead. However, there is some indication that these radical and cationic species can be generated from **1** and trapped with agents other than **1** itself, since the electrochemical oxidation of **1** may yield dimeric tetrahydronaphthalene derivatives.[12] No trimeric products were reported under these highly polar, electrochemical conditions. Therefore, this type of sequential radical-cation Diels–Alder reaction followed by trapping of the resulting radical or cationic species to form hydroxytetrahydronaphthalenes remains a most intriguing synthetic challenge.

Conclusions

The work reported here establishes a correlation between radical-cation Diels–Alder chemistry and the stereochemistries of the lignans galbulin and isogalbulin. However, the observation of the trimers **9–13** and regioisomer products **8**, **14**, and **15**, which have not been observed in nature, precludes any straightforward correlation of this radical-cation chemistry with the biosynthesis of the lignans. From a synthetic prospective, these propenylbenzene Diels–Alder reactions are reasonably efficient processes, albeit stereochemically quite complex. Nevertheless, with appropriate stereochemical constraints, these reactions might be applied to significant advantage in the construction of lignans. We are currently exploring methods by which this might be achieved.

Experimental Section

Reaction of Methylisoeugenol with Tris(*p*-bromophenyl)aminium Hexachloroantimonate (BAHA). To a solution of *trans*-methylisoeugenol (**1**; 59.1 mg, 0.331 mmol; obtained by preparative GLC) in 20 mL of dichloromethane under an argon atmosphere was added sodium carbonate (1.054 g, 9.95 mmol) followed by BAHA[13] (175.7 mg, 0.215 mmol). After the resultant mixture was stirred at room temperature for 16 h, the bluish color of the BAHA had faded. At this time, the light brown reaction mixture was passed through a small column of silica gel (230–400 mesh, 20 × 60 mm) eluting with 100 mL of ethyl acetate/hexanes, 1:1. The eluent displayed five spots on TLC (ethyl acetate/hexanes, 4:6) and 11 peaks upon HPLC analysis (silica gel column, 4.5 × 250 mm, gradient elution from 2% ethyl acetate/dichloromethane to 4% ethyl acetate/dichloromethane over 15 min). The substances associated with these 11 HPLC peaks were isolated by means of a preliminary column chromatography (silica gel, 230–400 mesh, 25% ethyl acetate/hexanes) to afford four fractions more polar than the tris(*p*-bromophenylamine). Final purification was achieved by preparative HPLC (silica gel, 10 × 250 mm, 4% ethyl acetate/dichloromethane) to obtain in order of relative polarity (least polar to most polar) **8**, **7**, 6, **14**, **13**, **11**, **10**, **15**, **9**, and **12**.

1α-(3,4-Dimethoxyphenyl)-2β-methyl-3β-ethyl-5,6-dimethoxyindan (6). The yield of **6** was determined to be 26% by HPLC analysis. Upon recrystallization from methanol, **6** was obtained as colorless crystals: mp 84.0 and 106.7–107.6 °C (lit.[6a] mp 96–97 and 105–107 °C); IR (KBr) 2940–2850, 1585, 1500, 1450, 1400, 1245, 1205, 1130, 1020, 980, 850, 840, 800, 745 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (dd, J = 7.2, 7.2 Hz, 3 H), 1.05 (d, J = 7.2 Hz, 3 H), 1.4 (ddq, J = 7.2, 9.3, 13.2 Hz, 1 H), 1.72 (ddq, J = 5.4, 7.2, 13.2 Hz, 1 H), 2.46 (ddq, J = 7.2, 7.2, 9.6 Hz, 1 H), 2.93 (ddd, J = 5.4, 7.2, 9.3 Hz, 1 H), 3.37 (s, 3 H), 3.79 (d, J = 9.6 Hz, 1 H), 3.81 (s, 3 H), 3.89 (s, 3 H), 3.90 (s, 3 H), 6.44 (s, 1 H), 6.64 (d, J = 2.1 Hz, 1 H), 6.71 (dd, J = 2.1, 8.1 Hz, 1 H), 6.81 (s, 1 H), 6.83 (d, J = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.03, 13.57, 22.17, 48.28, 49.37, 55.58, 56.72, 107.90, 110.64, 111.02, 120.58, 136.44, 137.88, 139.17, 147.39, 147.84, 148.62; HRMS, m/z calcd for $C_{22}H_{28}O_4$ (M^+) 356.1987, found 356.1996.

1-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-2,3-dimethylnaphthalene (7). The yield of **7** was determined to be ~1% by HPLC analysis. Upon recrystallization from methanol, **7** was obtained as colorless plates: mp 178–179 °C (lit.[9] mp 178–179 °C); IR (KBr) 2905, 2810, 1600, 1570, 1500, 1445, 1400, 1305, 1235, 1210, 1185, 1150, 1125, 1020, 885, 870, 825, 805, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3 H), 2.35 (s, 3 H), 3.86 (s, 3 H), 3.95 (s, 3 H), 4.02 (s, 3 H), 4.03 (s, 3 H), 6.72 (d, J = 1.8 Hz, 1 H), 6.74 (dd, J = 1.8, 7.8 Hz, 1 H), 6.95 (d, J = 7.8 Hz, 1 H), 7.10 (s, 1 H), 7.23 (s, 1 H), 7.46 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.82, 21.74, 55.82, 103.44, 106.25, 110.91, 112.69, 121.59, 124.44, 126.57, 128.57, 130.39, 132.98, 134.47, 138.42, 147.54, 148.65, 148.87, 149.09; HRMS, m/z calcd for $C_{22}H_{24}O_4$ (M^+) 352.1674, found 352.1676.

2-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-1,3-dimethylnaphthalene (8). The yield of **8** was determined to be ~8% by HPLC analysis. Upon recrystallization from methanol, **8** was obtained as colorless plates: mp 164–164.5 °C; IR (KBr) 2900, 1600, 1570, 1490, 1425, 1390, 1225, 1150, 1130, 1000, 940, 880, 860, 805, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12 (s, 3 H), 2.45 (s, 3 H), 3.70 (s, 3 H), 3.86 (s, 3 H), 3.99 (s, 6 H), 6.67 (s, 1 H), 6.78 (d, J = 1.8 Hz, 1 H), 6.10 (dd, J = 1.8, 9.9 Hz, 1 H), 7.01 (d, J = 9.9 Hz, 1 H), 7.06 (s, 1 H), 7.51 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.46, 21.01, 55.57, 55.83, 105.34, 105.59, 111.07, 113.17, 122.27, 125.79, 127.34, 127.53, 131.54, 133.23, 133.55, 136.98, 147.66, 148.50, 148.69; HRMS, m/z calcd for $C_{22}H_{24}O_4$ (M^+) 352.1674, found 352.1640.

1β,5α-Di-(3,4-dimethoxyphenyl)-2α,3α,4β-trimethyl-7,8-dimethoxy-1,2,2a(*Hα*),3,4,5-hexahydroacenaphthylene (9). The yield of **9** was determined to be 3% by HPLC analysis. Upon recrystallization from methanol, **9** was obtained as a colorless solid: mp 160–162 °C; IR (KBr) 2910, 2860, 1590, 1510, 1480, 1460, 1380, 1350, 1250, 1135, 1020, 800 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), δ 0.95 (d, J = 6.3 Hz, 3 H), 1.18 (d, J = 6.3 Hz, 3 H), 1.30 (d, J = 6.3 Hz, 3 H), 1.55 (ddq, J = 6.3, 9.6, 10.2 Hz, 1 H), 1.72 (ddq, J = 6.3, 10.2, 10.2 Hz, 1 H), 2.15 (ddq, J = 6.3, 9.6, 9.6 Hz, 1 H), 2.45 (dd, J = 9.6, 9.6 Hz, 1 H), 3.22 (s, 3 H), 3.47 (d, J = 10.2 Hz, 1 H), 3.57 (s, 3 H), 3.81 (d, J = 9.6 Hz, 1 H), 3.85 (s, 6 H), 3.87 (s, 3 H), 3.89 (s, 3 H), 6.15 (s, 1 H), 6.65–6.85 (c, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.94, 18.83, 43.11, 45.30, 53.99, 54.10, 55.87, 55.97, 56.25, 58.26, 59.86, 110.79, 111.37, 111.74, 112.08, 120.62, 121.85, 131.95, 135; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2843.

1α,5α-Di-(3,4-dimethoxyphenyl)-2β,3α,4β-trimethyl-7,8-dimethoxy-1,2,2a(*Hα*),3,4,5-hexahydroacenaphthylene (10). The yield of **10** was determined to be 14% by HPLC analysis. Upon recrystallization from methanol, **10** was obtained as colorless prisms: mp 126–127 °C; IR (KBr) 2915, 2815, 1590, 1510, 1460, 1415, 1345, 1255, 1225, 1190, 1135, 1020, 960, 840, 830, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, J = 6.5 Hz, 3 H), 0.95 (d, J = 7.2 Hz, 3 H), 0.97 (d, J = 6.5 Hz, 3 H), 1.44 (ddq, J = 7.2, 10.5, 10.8 Hz, 1 H), 1.65 (ddq, J = 6.5, 10.5, 10.5 Hz, 1 H), 2.62 (dq, J = 6.5, 6.3 Hz, 1 H), 2.96 (ddd, J = 1.8, 6.3, 10.8 Hz, 1 H), 3.41 (dd, J = 10.5, 1.8 Hz, 1 H), 3.58 (s, 3 H), 3.63 (s, 3 H), 3.85 (s, 3 H), 3.86 (s, 6 H), 3.9 (s, 3 H), 4.12 (s, 1 H), 6.17 (s, 1 H), 6.6–6.9 (c, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.90, 16.80, 36.23, 44.96, 47.22, 48.39, 53.45, 55.78, 60.41, 110.81, 111.18, 111.27, 112.29, 118.92, 121.62, 133.56, 134.57, 135.50, 136.60, 138.59, 144.68, 147.30, 148.62, 151.79; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2828.

1α,5β-Di-(3,4-dimethoxyphenyl)-2β,3α,4α-trimethyl-7,8-dimethoxy-1,2,2a(*Hα*),3,4,5-hexahydroacenaphthylene (11). The yield of **11** was determined to be 4% by HPLC analysis. Upon recrystallization from methanol, **11** was obtained as a colorless solid: mp 104–106 °C; IR (KBr) 2905, 1600, 1580, 1505, 1480, 1445, 1260, 1225, 1130, 1020, 850, 800 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), δ 0.8 (d, J = 6.9 Hz, 3 H), 0.98 (d, J = 6.9 Hz, 3 H), 1.09 (d, J = 7.2 Hz, 3 H), 1.76 (ddq, J = 2.7, 6.9, 11.7 Hz, 1 H), 1.9 (dq, J = 2.7, 7.2 Hz, 1 H), 2.53 (dq, J = 6.0, 6.9 Hz, 1 H), 2.86 (dd, J = 6.0, 11.7 Hz, 1 H), 3.58 (s, 3 H), 3.73 (s, 3 H), 3.75 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 3.93 (s, 1 H), 4.17 (s, 1 H), 6.55–6.8 (c, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.70, 16.05, 16.85, 26.15, 42.82, 43.43, 46.99, 47.43, 55.78, 56.01, 58.69, 59.73, 109.11, 110.54, 111.06, 111.17, 111.95, 119.26, 120.31, 129.55, 135.44, 137.00, 137.24, 140.87, 146.70, 147.40, 148.31, 148.90, 152.26; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2811.

1β,5β-Di-(3,4-dimethoxyphenyl)-2α,3α,4α-trimethyl-7,8-dimethoxy-1,2,2a(*Hα*),3,4,5-hexahydroacenaphthylene (12). The yield of **12** was determined to be 3% by HPLC analysis. Upon recrystallization from methanol, **12** was obtained as a colorless solid: mp 124–126 °C; IR (KBr) 2940, 2870, 2830, 1590, 1510, 1480, 1455, 1410, 1350, 1255, 1230, 1130, 1220, 840, 800, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ

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1.02 (d, J = 6.6 Hz, 3 H), 1.12 (d, J = 6.9 Hz, 3 H), 1.23 (d, J = 6.3 Hz, 3 H), 1.86 (c, 2 H), 2.09 (ddq, J = 6.3, 9.3, 9.9 Hz, 1 H), 2.31 (dd, J = 9.9, 10.3 Hz, 1 H), 3.3 (s, 3 H), 3.67 (s, 3 H), 3.79 (d, J = 9.3 Hz, 1 H), 3.8 (s, 3 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 3.89 (s, 1 H), 6.35–6.85 (c, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.82, 17.88, 18.33, 32.88, 44.97, 48.43, 51.21, 55.07, 55.61, 55.86, 56.14, 57.87, 59.94, 110.73, 111.06, 112.11, 112.22, 112.44, 120.32, 120.44, 128.60, 135.33, 136.75, 137.66, 140.96, 144.26, 147.04, 147.49, 148.39, 148.53, 152.41; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2831.

1β,5β-Di-(3,4-dimethoxyphenyl)-2β,3α,4α-trimethyl-7,8-dimethoxy-1,2,2a($H\alpha$),3,4,5-hexahydroacenaphthylene (13). The yield of **13** was determined to be 3% by HPLC analysis. Upon recrystallization from methanol, **13** was obtained as a colorless solid: mp 184–186 °C; IR (KBr) 2905, 1590, 1510, 1455, 1405, 1380, 1315, 1255, 1235, 1135, 1220, 975, 855 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, J = 6.9 Hz, 3 H), 1.03 (d, J = 6.3 Hz, 3 H), 1.06 (d, J = 6.9 Hz, 3 H), 1.85 (dq, J = 6.9, <4.0 Hz, 1 H), 1.91 (ddq, J = 6.3, 10.5, <4.0 Hz, 1 H), 2.54 (dq, J = 6.0, 6.9 Hz, 1 H), 2.83 (dd, J = 6.0, 10.5 Hz, 1 H), 3.23 (s, 3 H), 3.78 (s, 3 H), 3.79 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 3.86 (s, 3 H), 3.93 (s, 1 H), 4.16 (s, 1 H), 6.35–6.8 (c, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.74, 15.78, 16.80, 26.41, 42.51, 43.93, 47.18, 51.18, 55.84, 56.10, 60.50, 110.67, 110.91, 111.23, 112.13, 112.78, 119.12, 120.62, 130.06, 134.40, 136.34, 136.47, 140.87, 145.14, 146.97, 147.34, 148.35, 148.76, 152.19; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2831.

1α,4β-Di-(3,4-dimethoxyphenyl)-2β,3α,5α-trimethyl-7,8-dimethoxy-1,2,2a($H\alpha$),3,4,5-hexahydroacenaphthylene (14). The yield of **14** was determined to be 19% by HPLC analysis. Upon recrystallization from methanol, **14** was obtained as a colorless solid: mp 131–132 °C; IR (KBr) 2905, 2820, 1590, 1510, 1490, 1460, 1415, 1260, 1240, 1140, 1025, 800 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), δ 0.61 (d, J = 6.6 Hz, 3 H), 0.98 (d, J = 6.9 Hz, 3 H), 1.19 (d, J = 6.6 Hz, 3 H), 1.92 (ddq, J = 6.6, 10.8, 10.8 Hz, 1 H), 2.22 (dd, J = 10.2, 10.8 Hz, 1 H), 2.59 (dq, J = 6.3, 6.9 Hz, 1 H), 2.90 (dd, J = 6.3, 10.8 Hz, 1 H), 2.92 (dq, J = 6.6, 10.2 Hz, 1 H), 3.6 (s, 3 H), 3.84 (s, 3 H), 3.86 (s, 6 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 4.13 (s, 1 H), 6.59–6.82 (c, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.96, 17.57, 20.05, 35.26, 39.96, 47.02, 49.02, 55.69, 56.00, 58.02, 60.41, 109.41, 110.71, 111.28, 118.85, 134.37, 134.89, 135.09, 136.45, 136.96, 144.60, 147.19, 148.61, 148.81, 151.85; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2854.

1β,4β-Di-(3,4-dimethoxyphenyl)-2α,3α,5α-trimethyl-7,8-dimethoxy-1,2,2a($H\alpha$),3,4,5-hexahydroacenaphthylene (15). The yield of **15** was determined to be 12% by HPLC analysis. Upon recrystallization from methanol, **15** was obtained as a colorless solid: mp 168–169 °C; IR (KBr) 2910, 2860, 1590, 1510, 1485, 1460, 1350, 1260, 1230, 1160, 1135, 1020, 980, 850, 830, 810, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 6.6 Hz, 3 H), 1.22 (d J = 6.9 Hz, 3 H), 1.25 (d, J = 6.3 Hz, 3 H), 1.86 (ddq, J = 6.6, 10.2, 9.6 Hz, 1 H), 2.13 (ddq, J = 6.3, 9.3, 9.6 Hz, 1 H), 2.25 (dd, J = 10.2, 10.2 Hz, 1 H), 2.34 (dd, J = 9.6, 9.6 Hz, 1 H), 2.98 (dq, J = 10.2, 6.9 Hz, 1 H), 3.28 (s, 3 H), 3.8 (d, J = 9.3 Hz, 1 H), 3.8 (s, 3 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 6.68–6.86 (c, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.90, 18.56, 20.62, 40.66, 41.83, 54.08, 54.45, 55.83, 56.35, 58.24, 58.59, 59.96, 109.52, 110.86, 111.75, 120.61, 120.99, 132.95, 135.86, 136.58, 137.42, 143.89, 147.32, 147.43, 148.55, 148.98, 152.35; HRMS, m/z calcd for $C_{33}H_{40}O_6$ (M^+) 532.2825, found 532.2804.

Mercuration of Trimers 9, 11, and 14. To a cooled solution (−22 °C) of the trimer (50 mg, 0.094 mmol) in 20 mL of dichloromethane under an argon atmosphere was added 48 mg (0.113 mmol) of mercuric trifluoroacetate and the solution stirred for 1 h. The reaction mixture was slowly warmed to room temperature and stirred at room temperature for 4 h; 2 mL of a saturated methanol solution of lithium hydroxide was added and the solution stirred further at room temperature overnight. The reaction mixture was extracted with water (2 × 20 mL), the organic layer dried over magnesium sulfate, and the solvent evaporated to yield the crude mercurated product. The major mercurated product was purified by column chromatography (silica gel, 230–400 mesh, 20% ethyl acetate/hexanes) to obtain mercurated derivatives.

Monomercurated Derivative of Trimer 9. Upon recrystallization from methanol, the mercurated derivative of trimer **9** was obtained as colorless plates: 44.6 mg, 58%; mp 211–212 °C; IR (KBr) 2900, 2860, 2820, 1585, 1500, 1450, 1395, 1260, 1225, 1020, 855, 810, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (d, J = 6.3 Hz, 3 H), 1.16 (d, J = 6.3 Hz, 3 H), 1.31 (d, J = 6.3 Hz, 3 H), 1.57 (ddq, J = 6.3, 10.2, 9.9 Hz, 1 H), 1.69 (ddq, J = 6.3, 10.2, 10.2 Hz, 1 H), 2.15 (ddq, J = 6.3, 10.2, 9.9 Hz, 1 H), 2.49 (dd, J = 9.9, 9.9 Hz, 1 H), 3.26 (s, 3 H), 3.38 (d, J = 10.2 Hz, 1 H), 3.65 (s, 3 H), 3.83 (d, J = 10.2 Hz, 1 H), 3.84 (s, 3 H), 3.86 (s, 3 H), 3.89 (s, 3 H), 3.92 (s, 3 H), 6.55–6.95 (c, 6 H).

Dimercurated Derivative of Trimer 11. Upon recrystallization from methanol, the mercurated derivative of trimer **11** was obtained as colorless plates: 32.5 mg, 32%; mp 230–231 °C; IR (KBr) 2920, 2830, 1490, 1440, 1390, 1330, 1300, 1230, 1020, 960, 845, 800, 765, 730 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, J = 6.3 Hz, 3 H), 1.07 (d, J = 6.3 Hz, 3 H), 1.09 (d, J = 6.3 Hz, 3 H), 1.90 (c, 2 H), 2.58 (dq, J = 6.0, 6.3 Hz, 1 H), 2.75 (dd, J = 6.0, 11.1 Hz, 1 H), 3.76 (s, 1 H), 3.78 (s, 3 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 3.85 (s, 3 H), 3.86 (s, 3 H), 3.95 (s, 3 H), 4.31 (s, 1 H), 6.37 (dd, J = 1.8, 7.5 Hz, 1 H), 6.48 (d, J = 1.8 Hz, 1 H), 6.76 (s, 1 H), 6.78 (d, J = 7.5 Hz, 1 H), 6.98 (s, 1 H).

Monomercurated Derivative of Trimer 14. Upon recrystallization from methanol, the mercurated derivative of trimer **14** was obtained as colorless plates: 49.2 mg, 64%; mp 196–197 °C; IR (KBr) 2910, 2830, 1580, 1480, 1455, 1440, 1235, 1210, 1130, 1010, 855, 820, 800, 790, 760 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (d, J = 6.3 Hz, 3 H), 1.01 (d, J = 6.9 Hz, 3 H), 1.26 (d, J = 6.9 Hz, 3 H), 1.74 (ddq, J = 6.3, 10.5, 10.5 Hz, 1 H), 2.21 (dd, J = 10.5, 10.5 Hz, 1 H), 2.55 (dq, J = 6.9, 6.3 Hz, 1 H), 2.79 (dd, J = 6.3, 10.5 Hz, 1 H), 2.91 (dq, J = 6.9, 10.5 Hz, 1 H), 3.72 (s, 3 H), 3.86 (s, 3 H), 3.87 (s, 3 H), 3.88 (s, 3 H), 3.91 (s, 3 H), 3.94 (s, 3 H), 4.29 (s, 1 H), 6.67 (d, J = 1.5 Hz, 1 H), 6.72 (dd, J = 1.5, 8.4 Hz, 1 H), 6.74 (s, 1 H), 6.82 (d, J = 8.4 Hz, 1 H), 6.92 (s, 1 H), 6.96 (s, 1 H).

Preparation of *cis*-1,2-Di-(3,4-dimethoxyphenyl)-*anti*-*cis*-3,4-dimethylcyclobutane (16). A neat solution of methylisoeugenol (**1**) (2.92 g, 16.3 mmol) was degassed by the freeze–thaw method and irradiated under an atmosphere of argon at 310 nm for 7 days in a Rayonet photochemical reactor. The desired cyclobutane **16** (408 mg, 14%, 33% based upon recovered starting material) could be separated from unreacted methylisoeugenol (1.69 g, 58% recovery) and other minor photoproducts by flash chromatography eluting with 20% ethyl acetate/hexanes. **16** was recrystallized from pentane. **16**: mp 64.0–64.2 °C; IR ($CHCl_3$) 2960, 1510, 1460, 1250, 1215, 1140, 1020, 860, 810 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.19 (d, J = 6.6 Hz, 6 H), 2.80 (dq, J = 6.6, 5.0 Hz, 2 H), 3.43 (d, J = 5.0 Hz, 2 H), 3.62 (s, 6 H), 3.78 (s, 6 H), 6.34 (d, J = 2.0 Hz, 2 H), 6.56 (dd, J = 8.0, 2.0 Hz, 2 H), 6.65 (d J = 8.0 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.01, 34.37, 49.64, 55.55, 55.70, 110.47, 111.82, 119.85, 133.89, 146.88, 148.19; HRMS, m/z calcd for $C_{22}H_{28}O_4$ (M^+) 356.1987, found 356.1998.

Reaction of *cis*-1,2-Di-(3,4-dimethoxyphenyl)-*anti*-*cis*-3,4-dimethylcyclobutane (16) with Tris(*p*-bromophenyl)aminium Hexachloroantimonate (BAHA). A mixture of 69.8 mg (0.196 mmol) of the cyclobutane **16** and 622.7 mg (5.87 mmol) of sodium carbonate in 12 mL of dichloromethane was treated with 104 mg (0.127 mmol) of BAHA[13] under an argon atmosphere. After the resultant mixture was stirred at room temperature for 15 h, the bluish color of the BAHA had faded to light brown. The reaction was quenched by passing the reaction mixture through a short column of silica gel (230–400 mesh, 20 mm × 60 mm), eluting with 100 mL of ethyl acetate/hexanes (1:1). The eluent displayed six spots by TLC (ethyl acetate/hexanes, 1:1) and seven peaks by HPLC analysis (silica gel, 4.5 × 250 mm, gradient elution, 2% ethyl acetate/dichloromethane to 4% ethyl acetate/dichloromethane over 15 min). These substances were isolated as described above and their identities confirmed by comparison with the previously isolated materials. The yields of these products were determined by HPLC analysis: *trans*-methylisoeugenol (**1**), 19%; naphthalene **7**, 1%; acid-catalyzed dimer **6**, 15%; trimer **13**, 17%; trimer **11**, 19%; trimer **12**, 25%.

Molecular Modeling Calculations. The molecular modeling reported in this work was done with CHEM-X (July 1986 version), developed and distributed by Chemical Design Ltd., Oxford, England, on a MicroVAX II computer. The bond lengths and angles from known X-ray crystal structures were used whenever possible, and where these were not available, the initial structural parameters were estimated from the X-ray crystal data from closely related structures. The molecular mechanics force field expression used by CHEM-X is a simplified form of that used in Allinger's MM2 program in which all of the cross-terms and higher order terms have been removed and an alternative fast angle expression added. The dihedral angles reported in Table I were obtained from structures for which the molecular mechanics energy had been iteratively minimized.

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Supplementary Material Available: General and X-ray experimental sections, X-ray data for **10** and the mercurated derivatives of **9**, **11**, and **14**, figures listing the atomic numbering scheme and tables for each compound (**9**-1...**9**-7, **10**-1...**10**-7, etc), ((1) X-ray structure determination summary, (2) atomic positional parameters, (3) bond distances, (4) bond angles, (5) anisotropic temperature factors, (6) hydrogen positional parameters), molecular geometry data after molecular mechanics energy minimization for compounds **9–15**, figures listing the numbering scheme for these molecular modeling studies and tables (**9**-1MM and **9**-2MM, **10**-1MM and **10**-2MM, etc) [(-1MM) orthogonal positional parameters and (-2MM) bond lengths, bond angles, and torsion angles] (90 pages). Ordering information is given on any current masthead page.

Chiral Synthesis via Organoboranes. 20. Conversion of Boronic Esters of Essentially 100% Optical Purity to *B*-Alkyl-9-borabicyclo[3.3.1]nonanes of Very High Optical Purity. Synthesis of Optically Active Homologated Esters, Nitriles, and Ketones

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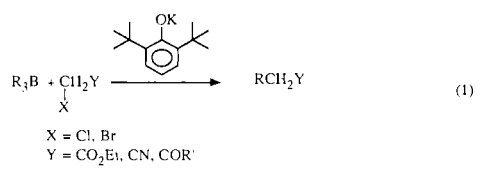
Abstract: 2-Alkyl-1,3,2-dioxaborinanes, $R^*BO_2(CH_2)_3$, of essentially 100% optical purity, prepared by the asymmetric hydroboration of readily available prochiral olefins with subsequent removal of the chiral auxiliary, can be transformed into lithium monoalkylborohydrides, R^*BH_3Li, of essentially 100% ee by reaction with lithium aluminum hydride. These borohydrides afford the corresponding monoalkylboranes, R^*BH_2, upon treatment with trimethylsilylchloride. Hydroboration of 1,5-cyclooctadiene with R^*BH_2 affords a mixture of *B*-alkyl-9-borabicyclo[4.2.1]nonane and *B*-alkyl-9-borabicyclo[3.3.1]nonane (*B*-R*-9-BBN). Thermal isomerization, 65 °C, 6 h, leads to isomerically pure *B*-R*-9-BBN without any significant loss of optical purity. The mixture of optically active *B*-alkyl-9-borabicyclo[4.2.1]nonane and *B*-R*-9-BBN react readily with ethyl bromoacetate, chloroacetonitrile, and α-bromo ketones in the presence of alkali metal *tert*-butoxide to give, respectively, homologated esters, nitriles, and ketones of very high optical purity. Since both (+)- and (-)-alkylboronic esters are available in essentially 100% optical purity, it is now possible to synthesize (+)- and (-)-esters, nitriles, and ketones in very high optical purities.

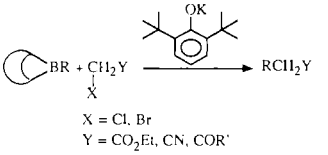
The ether-catalyzed addition of diborane to unsaturated organic molecules—the hydroboration reaction—made organoboranes readily available.[2] The boron atom in these organoboranes can be readily substituted with a variety of functional groups to give organic compounds under mild conditions such that organoboranes are now among the most versatile intermediates available to the organic chemist.[3] Our studies of these substitution reactions revealed that the organoboranes transfer the alkyl group to essentially most of the other elements of synthetic interest, including carbon, with complete retention of stereochemistry. For example, α-halogenated esters, nitriles, and ketones are readily alkylated with trialkylboranes in the presence of potassium 2,6-di-*tert*-butylphenoxide to give the corresponding homologated esters, nitriles, and ketones (eq 1).[4]



(1)

In attempting to apply this reaction to the synthesis of optically active derivatives, R^*CO_2R, R^*CH_2CN, and R^*CH_2COR', we were faced with several problems. First, this reaction involves utilization of only one of the three alkyl groups of the trialkylborane, R_3B. Use of symmetrical trialkylboranes in this reaction limits the maximum yield of products to 33.3%. Second, even if we were to accept utilization of only one-third of the optically active groups in the reagent, R^*_3B, we did not have available an established procedure for its synthesis.

Use of mixed organoboranes, such as RR'_2B in which group R shows significantly greater migratory aptitude is effective in circumventing this difficulty. It may be stated that selection of the most suitably mixed organoboranes is the key to the successful application of organoboranes to organic synthesis. Indeed, if *B*-alkyl-9-borabicyclo[3.3.1]nonane (*B*-R-9-BBN) derivatives are used in this α-alkylation reaction, a more economical utilization of the organic group introduced is achieved (eq 2).[4]



(2)

Consequently, it appeared that the *B*-R*-9-BBN derivatives might provide a satisfactory solution. However, we did not have available an established method for the synthesis of these derivatives. Accordingly, we had to devise some convenient procedure for the synthesis of *B*-R*-9-BBN and then attempt a quantitative

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