Cage Enlargement of 1,4-Bis(hydroxymethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane to a Tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonane System in Formic Acid

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Cationic rearrangement of 1,4-bis(diarylhydroxymethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octanes (**1**) in formic acid gave new cage compounds, 8,8-diaryl-2-diarylmethylene-*exo*-5-(formyloxy)tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonan-7-ols (**3**) and new cage-degradation products, 5,5-diaryl-4-[4-(diarylmethylene)-2-cyclobutenyl]-2-cyclopenten-1-ones (**4**) along with Wagner–Meerwein rearrangement products, pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanes (**5**; C_2-bishomocubanes) and pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decanes (**6**; D_{2h}-bishomocubanes). 9,9-Diaryl-4-(diarylhydroxymethyl)pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-1-ols (**2**) gave **4**, **5**, and **6** without the formation of **3**. A Wagner–Meerwein 1,2-bond shift of **1** gave key intermediates **2** which were converted into **3** via homoallylic rearrangement, into **4** via pinacol–pinacolone-like rearrangement, or into **5** and **6** via Wagner–Meerwein rearrangement.

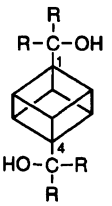
In our previous paper, we described the cationic rearrangement of 4-homocubanemethanols bearing diaryl groups on the α-carbon atom, giving a mixture of pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (C_2-bishomocubane) and pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (D_{2h}-bishomocubane).[1] To our surprise, the cationic rearrangement of 1,4-bis(hydroxydiphenylmethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (**1a**) in formic acid gave a new cage compound, *exo*-5-formyloxy-8,8-diphenyl-2-(diphenylmethylene)tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonan-7-ol (**3aa**) and a new cage-degradation product, 5,5-diphenyl-4-[4-(diphenylmethylene)-2-cyclobutenyl]-2-cyclopenten-1-one (**4a**) along with Wagner–Meerwein rearrangement products, C_2- and D_{2h}-bishomocubanes (Chart 1). We report here the results of our investigation on the cationic rearrangement of **1a—c** to **3**, **4**, **5**, and **6**. The cationic rearrangement of 9,9-diaryl-4-(diarylhydroxymethyl)pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-1-ols (**2aa**, **2ba**, and **2ca**), which may be one of the key intermediate products in the reaction of **1**, is also described.

Results and Discussion

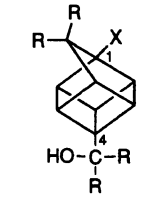
Compounds **1a—c** were prepared by reaction of dimethyl pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1,4-dicarboxylate (**7**)[2] with 4 molar amounts of corresponding Grignard reagents. 4-Homocubanemethanols (**2aa**, **2ba**, **2bc**, and **2ca**) were prepared from **7** in three steps. Methyl 4-(disubstituted hydroxymethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylates (**8a—c**), prepared from **7** with 2 molar amounts of the Grignard reagents, were treated with formic acid at room temperature to give methyl 1-(formyloxy)pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate (**9aa**, **9ba**, and **9ca**) in good yields (Chart 2). Compound **9bb** was prepared by reaction of **8b** with 0.3 molar amount of *p*-toluenesulfonic acid (*p*-TsOH) in methanol. Reaction of **9aa**, **9ba**, **9bb**, and **9ca** with 2 to 4 molar amounts of the Grignard reagents in tetrahydrofuran (THF) under reflux gave alcohols **2aa**, **2ba**, **2bc**, and **2ca** in moderate yields.

Synthesis and Separation of 3aa and 4a. Compound **1a** was allowed to react with formic acid for 12 h at room temperature, Separation of components in the reaction mixture by a combination of column and preparative thin-layer chromatographies on silica gel afforded two new compounds, new cage compound **3aa** and new cage-degradation product **4a** along with a mixture of C_2- and D_{2h}-bishomocubanes. Compound **3aa** was shown to have the formula $C_{35}H_{28}O_3$ from a mass spectral molecular ion peak at m/z 496 (M^+) and elemental analysis. Infrared spectrum [IR (KBr)] absorptions at 3570 and 1725 cm^{-1} indicated the existence of hydroxyl and carbonyl groups. In the proton nuclear magnetic resonance (^{1}H NMR) spectrum, **3aa** showed multiplets due to aromatic protons between δ=7.46 and 7.15. The downfield signal at δ=8.17 and the signal of the singlet proton at δ=5.47 were assigned to the proton of the formyl group at the 5-position and the proton on the carbon atom bearing the formyloxy group, respectively. Five aliphatic proton signals at δ=3.48 (2H, m), 3.35 (1H, m), and 2.79 (2H, m) assigned to the skeleton were observed. Ozonolysis of **3aa** gave benzophenone, indicating the existence of a diphenylmethylene group. The structure of **3aa** was finally confirmed by single-crystal X-ray analysis. The ORTEP drawing of **3aa** is shown in Fig. 1. Thus, the structure of **3aa** was determined to be *exo*-5-formyloxy-8,8-diphenyl-2-(diphenylmethylene)tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonan-7-ol.

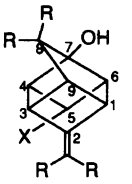
Compound **4a** was shown to have the formula $C_{34}H_{26}O$ from a mass spectral molecular ion peak at m/z 450 (M^+) and elemental analysis. An IR ($CHCl_3$) absorption at 1705 cm^{-1} and the appearance of carbonyl carbon resonance (δ=209.1) in the carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrum indicated the existence of a carbonyl group conjugated to



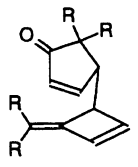
1a : R = C_6H_5
1b : R = $C_6H_4OCH_3$-4
1c : R = CH_3



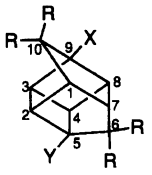
2aa : R = C_6H_5, X = OH
2ab : R = C_6H_5, X = OCHO
(not detected)
2ba : R = $C_6H_4OCH_3$-4, X = OH
2bb : R = $C_6H_4OCH_3$-4, X = OCHO
(not detected)
2bc : R = $C_6H_4OCH_3$-4, X = OCH_3
2ca : R = CH_3, X = OH



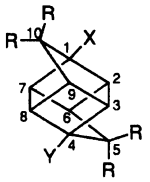
3aa : R = C_6H_5, X = OCHO
3ab : R = C_6H_5, X = OH
3ba : R = $C_6H_4OCH_3$-4, X = OCHO
3bb : R = $C_6H_4OCH_3$-4, X = OH



4a : R = C_6H_5
4b : R = $C_6H_4OCH_3$-4

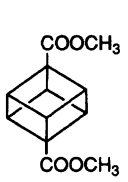


5aa : R = C_6H_5, X = Y= OCHO
5ab : R = C_6H_5, X = OCHO, Y = OH
5ac : R = C_6H_5, X = Y = OH
5ba : R = $C_6H_4OCH_3$-4, X = Y = OCHO
5bb : R = $C_6H_4OCH_3$-4, X = Y = OH
5bc : R = $C_6H_4OCH_3$-4, X = OCH_3, Y = OCHO
5ca : R = CH_3, X = Y = OCHO
5cb : R = CH_3, X = OCHO, Y = OH
5cc : R = CH_3, X = Y = OH



6aa : R = C_6H_5, X = Y= OCHO
6ab : R = C_6H_5, X = OCHO, Y = OH
6ac : R = C_6H_5, X = Y = OH
6ba : R = $C_6H_4OCH_3$-4, X = Y = OCHO
6bb : R = $C_6H_4OCH_3$-4, X = Y = OH
6bc : R = $C_6H_4OCH_3$-4, X = OCH_3, Y = OCHO
6ca : R = CH_3, X = Y = OH

Chart 1.



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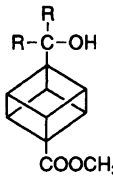
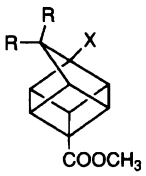


8a : R = C_6H_5
8b : R = $C_6H_4OCH_3$-4
8c : R = CH_3



9aa : R = C_6H_5, X = OCHO
9ba : R = $C_6H_4OCH_3$-4, X = OCHO
9bb : R = $C_6H_4OCH_3$-4, X = OCH_3
9ca : R = CH_3, X = OCHO

Chart 2.

a carbon–carbon double bond. The signals observed at δ=132.7 and 63.4 were assigned to *exo*-diphenylmethylene and diphenylmethyl groups, respectively. The ^{1}H NMR spectrum of **4a** showed signals due to aromatic protons between δ=7.5 and 6.9. Four olefinic proton signals were observed at δ=7.60 (dd, J=2.0 and 6.0 Hz), 6.46 (d, J=3.0 Hz), 6.23 (dd, J=2.0 and 6.0 Hz), and 5.46 (dd, J=1.0 and 3.0 Hz) and signals due to two methine protons appeared at δ=3.68 (bd, J=3.0 Hz) and 3.51 (dt, J=3.0 and 2.0 Hz). Ozonolysis of **4a** gave benzophenone, indicating the existence of a diphenylmethylene group. The assignment of these six protons could be achieved as partial molecular structures (**I**, **II**, and **III**) by decoupling techniques on the basis of IR, ^{1}H and ^{13}C NMR spectral data, and ozonolysis. As shown in Chart 3, the observed coupling constants (J=3.0 and 6.0 Hz) of the olefinic protons indicated the existence of nonfused four- and five-membered rings.[3] Accordingly, the structure of **4a** was elucidated as 5,5-diphenyl-4-[4-(diphenylmethylene)-2-cyclobutenyl]-2-cyclopenten-

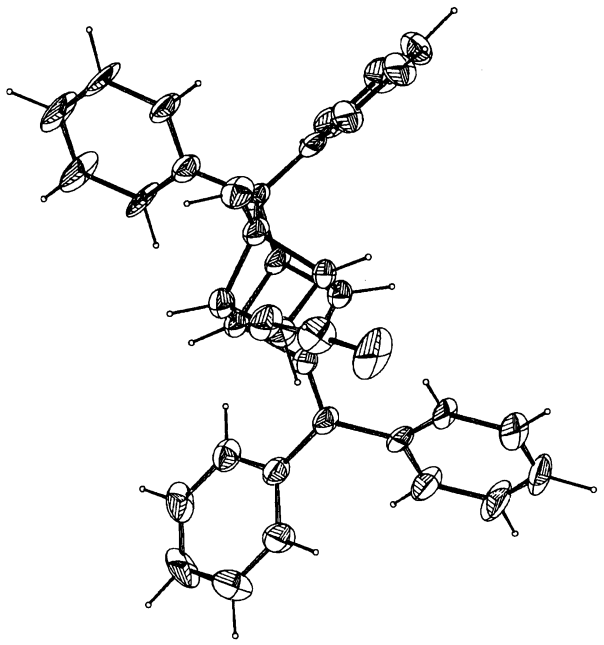
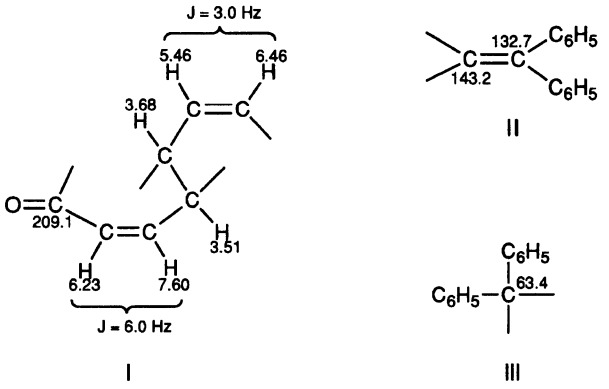


Fig. 1. ORTEP drawing of **3aa**.



I II III

Chart 3.

1-one.

In this reaction, the production of **5aa**, **5ab**, **5ac**, **6aa**, **6ab**, and **6ac** having C_2- and D_{2h}-bishomocubane skeletons was estimated[4] and direct attempts to separate the resulting products were unsuccessful. The products were then converted into the corresponding alcohols (**5ac** and **6ac**) by treatment with sodium methoxide in methanol. The structures of **5ac** and **6ac** were determined by elemental analysis, IR and NMR spectra.

Similar treatment of 1,4-bis[hydroxybis(4-methoxyphenyl)methyl]pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (**1b**) in formic acid was shown to give **3ba**, **5ba**, and **6ba** without giving **4b**. When 1,4-bis(1-hydroxy-1-methylethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (**1c**) was treated with formic acid, a mixture of C_2-bishomocubanes (**5ca**, **5cb**, and **5cc**) was obtained without the formation of compounds corresponding to **3** and **4**. D_{2h}-bishomocubanes were not obtained in this run. After treatment of the reaction mixture with sodium methoxide in methanol it was apparent that D_{2h}-bishomocubanes are formed along with C_2-bishomocubanes.

Rearrangement Reactions. To determine the scope of the rearrangement, we investigated the cationic rearrangement of **1** and **2** to **3**, **4**, **5**, and/or **6** under various conditions. Compounds **2aa** and **2ba** were considered to be intermediate products of the rearrangement of **1**, leading to **4a** and **4b** along with **5** and **6**. To account for the role of hydroxyl or *O*-formyl groups on the 1-position, reaction of **2bc** was attempted. Compound **2ca** was employed as a reference. All reactions of **1** and **2** with acids were carried out at room temperature and followed by thin-layer chromatography (TLC). Reactions of **1** and **2** with formic acid gave a mixture of an alcohol and its *O*-formyl derivatives. As it was difficult to separate the alcohol and the *O*-formyl derivatives in the reaction mixture by chromatographic procedures, the resulting products were separated as the corresponding alcohols after treatment with sodium methoxide in methanol. In this treatment, the *O*-formyl derivatives were converted into the corresponding alcohol derivatives in quantitative yields. In all runs, yields of **3**, **5**, and **6** were calculated on the basis of the amount of the respective alcohol derivatives, except for yields of **5bc** and **6bc**. *O*-formyl derivatives were not converted into corresponding alcohol derivatives in formic acid. These results are summarized in Tables 1 and 2.

When **1a** was treated with formic acid, **3ab**, **4a**, **5ac**, and **6ac** were obtained in 25%, 10%, 47%, and 13% yields, respectively. Reaction of **1a** with trifluoroacetic acid (TFA) in a (1:1) mixture of water and dichloromethane gave only **4a** in a 13% yield without the formation of **3ab**, **5ac**, and **6ac**. Reaction of **1b** with formic acid gave **3bb** in a 57% yield along with **5bb** (19%) and **6bb** (8%) without the formation of cage-degradation product **4b**. When **1b** was treated with 0.3 molar amount of *p*-TsOH in a (1:1) mixture of water and dichloromethane, cage-degradation product **4b** was obtained in a 10% yield without the formation of **3bb**, **5bb**, and **6bb**. When **1c** was treated with formic acid, the corresponding alcohol derivatives (**5cc** and **6ca**) were obtained in 82% and 8% yields, respectively, without giving a new cage product and a cage-degradation product corresponding to **3** and **4**. Similar treatment of **1c** with 0.3 molar amount of *p*-TsOH in a (1:1) mixture of water and dichloromethane afforded only a mixture of **5cc** and **6ca** in 80% and 8% yields, respectively.

Treatment of **2aa** with formic acid gave **4a**, **5ac**, and **6ac** without the formation of **3ab**. When **2ba** was treated with formic acid, **4b** was obtained along with **5bb** and **6bb**. The same treatment of **2bc** with formic acid gave only *O*-formyl derivatives (**5bc** and **6bc**) without the formation of **4b** and the corresponding alcohol derivatives. Therefore, both compounds were separated by chromatographic methods without treatment with sodium methoxide. Reaction of **2ca** with formic

Table 1. Cationic Rearrangement of **1**

Entry	Reactant	Conditions[a]			Product[e] (Yield/%)[f]
		Acid	Solvent	Time/h	
1	**1a**	HCOOH		12	**3ab** (25), **4a** (10), **5ac** (47), **6ac** (13)
2	**1a**	TFA[b]	H_2O/CH_2Cl_2[d]	18	**4a** (13)
3	**1b**	HCOOH		1	**3bb** (57), **4b** (—)[g], **5bb** (19), **6bb** (8)
4	**1b**	*p*-TsOH[c]	H_2O/CH_2Cl_2[d]	48	**4b** (10)
5	**1c**	HCOOH		12	**5cc** (82), **6ca** (8)
6	**1c**	*p*-TsOH[c]	H_2O/CH_2Cl_2[d]	12	**5cc** (80), **6ca** (8)

a) All experiments were carried out at room temperature. HCOOH was employed as a solvent in Entries 1, 3, and 5. b) TFA; 10 molar amounts of trifluoroacetic acid. c) *p*-TsOH; 0.3 molar amount of *p*-toluenesulfonic acid. d) H_2O/CH_2Cl_2; A (1 : 1) mixture of water and dichloromethane. e) Products shown in Entries 1, 3, and 5 were isolated as alcohol derivatives after treatment of formates with sodium methoxide in methanol. f)Isolated yield. g) —; not detected.

Table 2. Cationic Rearrangement of **2** in Formic Acid

Entry	Reactant	Conditions[a]	Product[b] (Yield/%)[c]
		Time/h	
1	**2aa**	12	**4a** (15), **5ac** (39), **6ac** (31)
2	**2ba**	1	**4b** (24), **5bb** (42), **6bb** (14)
3	**2bc**	1	**5bc** (34)[d], **6bc** (14)[d]
4	**2ca**	12	**5cc** (76), **6ca** (10)

a) All experiments were carried out at room temperature in formic acid. b) Products shown in Entries 1, 2, and 4 were isolated as alcohol derivatives after treatment of formates with sodium methoxide in methanol. c) Isolated yield. d) Yield of formate.

acid gave only a mixture of **5cc** and **6ca**.

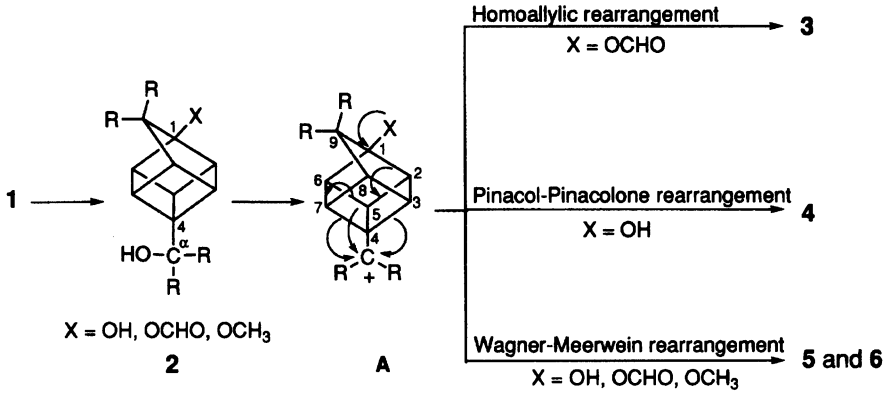
Although the observations that the system of **1** underwent a Wagner–Meerwein rearrangement to homocubane and bishomocubane systems is not surprising,[5] it was unexpected that **1** reacted readily with formic acid, giving new cage compounds **3** and new cage-degradation compounds **4** along with C_2- and D_{2h}-bishomocubane via **2**. In a cursory study of this reaction, it was apparent that the homocubane system bearing a hydroxyl group on the 1-position of **2aa** and **2ba** gives **4** and the homocubane system bearing an *O*-formyl group on the 1-position of **2ab** and **2bb**, which have not been detected yet, gives **3** along with C_2- and D_{2h}-bishomocubanes.

Schemes 1 and 2 depict a mechanistic scheme, which accounts for our observations of these rearrangements. First, **1** rearrange to 4-homocubanemethanols **2** via Wagner–Meerwein rearrangement. The rearrangement into the homocubane system is driven by the release of strain energy of about 40 kcal mol^{-1}. Then, reaction of **2** with acid gives carbocation intermediates **A**. When R is a phenyl group or a 4-methoxyphenyl group and X is a formyloxy group, **3** is formed via ring cleavage at the C_4–C_5 bond (homoallylic rearrangement) as shown in Scheme 2. In this case, the back-side attack on the C_5 atom by the carbonyl group in carbocation intermediate **B** accelerates ring cleavage, giving carbocation intermediate **C** which is converted via intermediate **D** into a tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonane system. When R is a phenyl group or a 4-methoxyphenyl group and substituent X is a hydroxyl group,[6] successive cleavage of the C_1–C_2, C_5–C_6, and C_4–C_7 bonds gives degradation products **4** via pinacol–pinacolone-like rearrangement. Carbocation **A** always gives C_2- and D_{2h}-bishomocubanes indicating that ring cleavage of the C_3–C_4 bond (or the equivalent the C_4–C_7 bond) and the C_4–C_5 bond via a Wagner–Meerwein 1,2-bond shift has occurred.

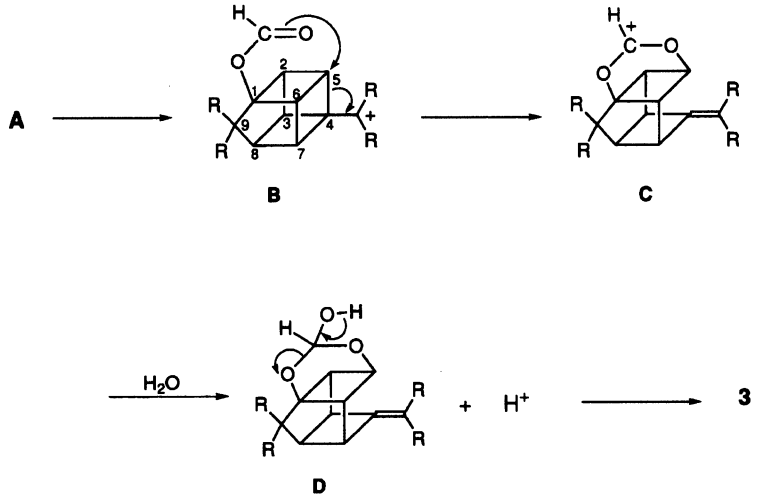
In these rearrangement reactions, both carbocation-stabilizing groups such as phenyl or 4-methoxyphenyl groups on the α-carbon atom and the X group on the 1-position of carbocation **A** may play major roles in the determination of the direction of the cage fission process to **3** and **4**. Stabilization of carbocation **A** by an R group on the α-carbon atom will relatively increase the production of D_{2h}-bishomocubanes.

Experimental

Melting points were measured in a Gallenkamp melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 260-30 infrared spectrophotometer and ^{1}H NMR and ^{13}C NMR spectra were measured on Hitachi R-90 (90 MHz), JEOL JNM-EX 270 (270 MHz), and Bruker AM 360 (360 MHz) spectrometers with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm (δ) and signals are described as s (singlet), d (doublet), t (triplet), m (multiplet), q (quartet), quin (quintet), or b (broad). All spectra were consistent with the assigned structures. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a JMS-DX 300 spectrometer operating at an ionization potential of 70 eV. Com-



Scheme 1.



Scheme 2.

bustion analyses were performed on a Perkin–Elmer Model 240C elemental analyzer.

1,4-Bis(hydroxydiphenylmethyl)pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane (1a). Half of a solution of bromobenzene (6.28 g, 40.0 mmol) in THF (160 ml) was added to a suspension of Mg (972 mg, 40.0 mmol) in THF (10 ml) under an atmosphere of argon. The mixture was warmed gently in order to initiate the reaction. The remainder of the THF solution was added dropwise in refluxing THF. The mixture was stirred for 1.5 h in refluxing THF and then cooled to room temperature. A solution of **7** (2.00 g, 9.09 mmol) in THF (55 ml) was added to this solution over 30 min. The resulting mixture was stirred for 1.5 h in refluxing THF, poured into ice-water, the pH being held at 3, and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with ice-water, 1 M NaOH (1 M=1 moldm^{-3}), and brine, successively, dried over $MgSO_4$ and evaporated to give an oily product, which was triturated with MeOH to give **1a** as crystals. Recrystallization from $CHCl_3$ gave pure **1a** as colorless prisms. Yield: 2.66 g (63%); mp 241.7—242.9 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.31—7.21 (20H, m), 3.91 (6H, s), and 2.12 (2H, b); ^{13}C NMR (90 MHz, $CDCl_3$) δ=144.2, 128.1, 127.1, 126.7, 78.6, 63.5, and 43.6; IR (KBr) 3600, 3020, 2980, 2960, 2880, 2850, 1495, 1455, and 1315 cm^{-1}; MS *m/z* 468 (M^+). Found: C, 86.31; H, 6.14%. Calcd for $C_{34}H_{28}O_2 \cdot 1/4\ H_2O$: C, 86.32; H, 6.07%.

1,4-Bis[hydroxybis(4-methoxyphenyl)methyl]pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (1b). This compound was prepared from **7** and 4-methoxyphenylmagnesium bromide according to the procedure employed for the preparation of **1a**. Yield: 74%; Colorless prisms (from a mixture of $CHCl_3$ and hexane); mp 296.0—297.0 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.15·6.80 (16H, A_2B_2q, J=8.8 Hz), 3.86 (6H, s), 3.77 (12H, s), and 2.06 (2H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ=158.5, 136.7, 127.9, 113.4, 78.0, 63.7, 55.2, and 43.5; IR ($CHCl_3$) 3600, 3020, 2840, 1610, 1585, 1515, 1465, 1445, 1415, and 1300 cm^{-1}; MS *m/z* 588 (M^+). Found: C, 66.01; H, 5.36; Cl, 15.33%. Calcd for $C_{38}H_{36}O_6 \cdot CHCl_3$: C, 66.15; H, 5.23; Cl, 15.05%.

1,4-Bis(1-hydroxy-1-methylethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (1c). This compound was prepared from **7** and methylmagnesium iodide according to the procedure employed for the preparation of **1a**. In this reaction ether was used as a solvent. Yield: 92%; Colorless needles (from $CHCl_3$); mp 172.2—173.6 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.71 (6H, s), 1.28 (2H, b), and 1.16 (12H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ=70.4, 65.9, 41.8, and 22.7; IR ($CHCl_3$) 3610, 2980, 1460, 1385, and 1370 cm^{-1}; MS *m/z* 220 (M^+). Found: C, 76.18; H, 8.96%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

4-(Hydroxydiphenylmethyl)-9,9-diphenylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-1-ol (2aa). A solution

of **9aa** (540 mg, 1.45 mmol) in THF (10 ml) was added to Grignard reagent, prepared from Mg (141 mg, 5.80 mmol), bromobenzene (910 mg, 5.80 mmol), and THF (20 ml). The mixture was stirred for 2 h in refluxing THF and treated according to the procedure employed for the preparation of **1a** to give crude crystals of **2aa**. Recrystallization from a mixture of $CHCl_3$ and hexane gave pure **2aa**. Colorless prisms; mp 212.0—215.0 °C. Yield: 580 mg (86%); ^{1}H NMR (270 MHz, $CDCl_3$) δ=7.31—7.11 (20H, m), 3.56 (1H, m), 3.42 (2H, m), 3.23 (3H, m), 2.23 (1H, s), and 2.13 (1H, s); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=144.4, 141.1, 128.23, 128.16, 128.07, 127.1, 126.6, 126.2, 91.1, 78.2, 67.2, 56.2, 49.0, 45.2, 42.4, and 40.7; IR ($CHCl_3$) 3560, 3400, and 2970 cm^{-1}; MS m/z 468 (M$^+$). Found: C, 87.18; H, 6.16%. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02%.

4-[Hydroxybis(4-methoxyphenyl)methyl]-9,9-bis(4-methoxyphenyl)pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-1-ol (2ba). This compound was prepared from **9ba** and 4-methoxyphenylmagnesium bromide according to the procedure employed for the preparation of **2aa** to give crude **2ba** as an oily material. This was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give pure **2ba** as a pale yellow oil. Yield: 58%; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.20·6.76 (8H, A_2B_2q, J=8.9 Hz), 7.19·6.82 (8H, A_2B_2q, J=8.9 Hz), 3.79 (6H, s), 3.74 (6H, s), 3.51 (1H, m), 3.38 (2H, m), 3.19 (2H, m), 3.14 (1H, m), 2.16 (1H, b), and 2.01 (1H, b); ^{13}C NMR (90 MHz, $CDCl_3$) δ=158.5, 157.8, 137.0, 133.5, 129.2, 127.8, 113.6, 113.4, 91.4, 77.6, 66.0, 56.4, 55.2, 55.1, 49.2, 45.2, 42.5, and 40.5; IR (KBr) 3450, 2960, 2840, 1615, 1585, 1515, 1465, and 1445 cm^{-1}; MS m/z 588 (M$^+$). Found: m/z 588.2548. Calcd for $C_{38}H_{36}O_6$: M, 588.2510.

4-[Hydroxybis(4-methoxyphenyl)methyl]-1-methoxy-9,9-bis(4-methoxyphenyl)pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (2bc). This compound was prepared from **9bb** and 4-methoxyphenylmagnesium bromide according to the procedure employed for the preparation of **2aa**. Yellow oil. Yield: 98%; ^{1}H NMR (270 MHz, $CDCl_3$) δ= 7.22·6.72 (8H, A_2B_2q, J=8.9 Hz), 7.20·6.81 (8H, A_2B_2q, J=8.9 Hz), 3.78 (6H, s), 3.72 (6H, s), 3.57 (3H, s), 3.48 (2H, m), 3.40 (3H, m), 3.16 (1H, m), and 2.03 (1H, b); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=158.4, 157.6, 137.0, 133.9, 129.6, 127.8, 113.3, 113.0, 97.1, 77.5, 67.2, 56.3, 55.2, 55.0, 48.9, 43.0, 42.4, and 41.6; IR ($CHCl_3$) 3580, 2980, and 1605 cm^{-1}; MS m/z 602 (M$^+$). Found: C, 77.78; H, 6.47%. Calcd for $C_{39}H_{38}O_6$: C, 77.72; H, 6.35%.

4-(1-Hydroxy-1-methylethyl)-9,9-dimethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-1-ol (2ca). This compound was prepared from **9ca** and methylmagnesium iodide according to the procedure employed for the preparation of **2aa**. Colorless needles (from $CHCl_3$); mp 127.8—129.8 °C. Yield: 88%; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.20 (3H, m), 3.03 (2H, m), 2.53 (1H, s), 2.49 (1H, t, J=6.0 Hz), 1.13 (6H, s), 0.76 (1H, s), and 0.74 (6H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ=91.9, 70.1, 56.8, 52.3, 49.0, 43.6, 40.5, 37.3, 23.6, and 13.7; IR (KBr) 3400, 3340, and 2970 cm^{-1}; MS m/z 220 (M$^+$). Found: C, 76.23; H, 9.13%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

Reaction of 1a with Formic Acid. Preparation of *exo*-5-Formyloxy-8,8-diphenyl-2-(diphenylmethylene)tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonan-7-ol (3aa), 5,5-Diphenyl-4-[4-(diphenylmethylene)-2-cyclobuten-yl]-2-cyclopenten-1-one (4a), 6,6,10,10-Tetraphenylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-5,9-diol (5ac), and 5,5,10,10-tetraphenylpentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane-1,4-diol (6ac). A solution of **1a** (500 mg, 1.07 mmol) in formic acid (20 ml) was stirred at room temperature for 12 h, then poured into ice-water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated to give an oily material. The oil was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give three fractions. The first fraction contained **4a**, the second fraction contained a mixture of **5aa**, **5ab**, **5ac**, **6aa**, **6ab**, and **6ac** which were separated as alcohol derivatives **5ac** and **6ac** by preparative thin-layer chromatography on silica gel with $CHCl_3$ as a developing solvent, after treatment with sodium methoxide in methanol. The third fraction contained **3aa**.

3aa: Yield: 20%; Colorless prisms (from a mixture of ether and hexane); mp 226.2—228.2 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=8.17 (1H, s), 7.46—7.15 (20H, m), 5.47 (1H, s), 3.48 (2H, m), 3.35 (1H, m), 3.20 (1H, bs), and 2.79 (2H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=160.0, 141.4, 139.9, 135.9, 129.2, 128.5, 128.3, 128.1, 126.9, 126.4, 126.2, 96.3, 77.8, 60.0, 53.4, 49.5, and 48.0; IR (KBr) 3570, 3530, and 1725 cm^{-1}; MS m/z 496 (M$^+$). Found: C, 84.81; H, 5.80%. Calcd for $C_{35}H_{28}O_3$: C, 84.65; H, 5.68%.

4a: Yield: 9%; Yellow oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.60 (1H, dd, J=6.0 and 2.0 Hz), 7.47—6.90 (20H, m), 6.46 (1H, d, J=3.0 Hz), 6.23 (1H, dd, J=6.0 and 2.0 Hz), 5.46 (1H, dd, J=3.0 and 1.0 Hz), 3.68 (1H, bd, J=3.0 Hz), and 3.51 (1H, dt, J=3.0 and 2.0 Hz); ^{13}C NMR (90 MHz, $CDCl_3$) δ=209.1, 163.5, 145.6, 143.2, 141.6, 140.7, 140.2, 140.1, 137.5, 132.7, 130.0, 129.7, 129.3, 128.6, 128.4, 128.3, 128.0, 127.9, 127.6, 127.4, 127.1, 126.8, 126.7, 63.4, 51.0, and 49.0; IR ($CHCl_3$) 1705 cm^{-1}; MS m/z 450 (M$^+$). Found: m/z 450.1991. Calcd for $C_{34}H_{26}O$: M, 450.1982. Found: C, 84.23; H, 5.42%. Calcd for $C_{34}H_{26}O$·1/3$CHCl_3$: C, 84.09, H, 5.41%.

5ac (40%) and 6ac (20%): Analytical data are shown in Tables 3 and 4.

Single-Crystal X-Ray Analysis of 3aa. Compound **3aa** was recrystallized from a mixture of ether and hexane at room temperature and air-dried to give colorless prisms containing two molecules of ether in the unit cell; triclinic space group $P\bar{1}$ with cell dimensions, a=13.123(3), b=12.721(2), c=9.631(2) Å, α=81.06(2), β=103.36(2), γ=95.53(2)°, Z=2. Diffracted intensities were recorded at room temperature on a Rigaku AFC-5FOS four-circle diffractometer (ω–2θ scan, 2θ<55°, Mo(Kα), λ=0.71069 Å). The structure was solved by a direct method (MULTAN-84),[7] and refined by a block-diagonal least-squares method.[8] The R factor and R_w-factor were 0.063 and 0.059, respectively. The ORTEP drawing[9] is shown in Fig. 1.

8, 8- Diphenyl- 2- (diphenylmethylene)tetracyclo-[4.3.0.0^{3,9}.0^{4,7}]nonane-*exo*-5,7-diol (3ab). Several drops of 28% sodium methoxide methanol solution were added to a solution of **3aa** (100 mg, 0.2 mmol) in methanol (10 ml). The mixture was stirred for 30 min at room temperature, then neutralized with 1 M HCl. After removal of the methanol, the residue was dissolved in CH_2Cl_2 and washed with brine, then dried over $MgSO_4$ and evaporated to give crude **3ab**. Recrystallization from a mixture of CH_2Cl_2

Table 3. Bishomocubane Derivatives **5** and **6**

Compd. no.	Appearance	Recryst. solv.	Mp (°C)	Formula	Anal. Found (Calcd)	
					C	H
5ac	Colorless powder	—	148.0—152.0	$C_{34}H_{28}O_2$	HRMS 468.2111[a] (468.2088)	
5ba	Colorless crystals	AcOEt–hexane	300.4—300.8	$C_{40}H_{36}O_8$	74.46 (74.52)	5.66 5.63)
5bb	Colorless powder	—	140.0—143.0	$C_{38}H_{36}O_6 \cdot 1/2H_2O$	76.59 (76.36)	6.21 6.24)
5bc	Colorless crystals	$CHCl_3$–hexane	293.5—294.6	$C_{40}H_{38}O_7 \cdot 1/4CHCl_3$	73.52 (73.18)	5.82 5.84)
5ca	Colorless crystals	Hexane	122.3—123.4	$C_{16}H_{20}O_4$	69.27 (69.55)	7.06 7.30)
5cb	Colorless oil	—	—	$C_{15}H_{20}O_3$	HRMS 248.1432[a] (248.1411)	
5cc	Colorless crystals	$CHCl_3$	211.2—214.2	$C_{14}H_{20}O_2$	76.08 (76.33)	8.96 9.15)
6ac	Colorless prisms	Acetone	295.0—297.0	$C_{34}H_{28}O_2$	87.14 (87.15)	6.07 6.02)
6ba	Colorless crystals	AcOEt	291.7—292.7	$C_{40}H_{36}O_8$	74.31 (74.52)	5.52 5.63)
6bb	Colorless crystals	Acetone	272.0—273.0	$C_{38}H_{36}O_6$	78.01 (77.53)	5.54 6.16)
6bc	Colorless crystals	$CHCl_3$–hexane	288.4—289.5	$C_{40}H_{38}O_7 \cdot 1/5CHCl_3$	73.77 (73.76)	5.47 5.88)
6ca	Colorless scales	$CHCl_3$	200.0—203.0	$C_{14}H_{20}O_2 \cdot 1/3H_2O$	74.24 (74.30)	9.07 9.20)

a) High-resolution mass spectrum.

and hexane gave **3ab** as colorless fine needles. Yield: 94 mg (100%); mp 221.8—223.4 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$) δ=7.44—7.12 (20H, m), 4.61 (1H, s), 4.03 (1H, bs), 3.14 (2H, dd, J=7.0 and 4.0 Hz), 3.28 (1H, t, J=4.0 Hz), 3.20 (1H, bs), and 2.58 (2H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=141.6, 140.0, 137.6, 129.1, 128.4, 128.2, 128.1, 127.9, 126.7, 126.3, 97.0, 75.6, 59.5, 53.2, 50.8, and 47.4; IR (KBr) 3500, 3060, 3040, and 1605 cm^{-1}; MS m/z 468 (M^+). Found: C, 87.41; H, 5.95%. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02%.

Reaction of 1a with TFA. Preparation of 4a. A mixture of **1a** (50 mg, 0.107 mmol) and TFA (120 mg, 1.07 mmol) in a (1 : 1) mixture of water and CH_2Cl_2 (2 ml) was stirred for 18 h at room temperature. The mixture was poured into saturated aqueous $NaHCO_3$ (10 ml) and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated to give an oil. The oil was purified by preparative thin-layer chromatography on silica gel with $CHCl_3$ as a developing solvent. The band with an R_f value of around 0.7 gave pure **4a** (6 mg).

Reaction of 1b with Formic Acid. Preparation of *exo*-5-Formyloxy-8,8-bis(4-methoxyphenyl)-2-[bis(4-methoxyphenyl)methylene]tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonan-7-ol (3ba), 5,9-Diformyloxy-6,6,10,10-tetra(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (5ba), and 1,4-Diformyloxy-5,5,10,10-tetra(4-methoxyphenyl)pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (6ba). A solution of **1b** (500 mg, 0.85 mmol) in formic acid (20 ml) was stirred for 1 h at room temperature. The reaction mixture was then treated according to the procedure employed for the preparation of **3aa** to give an oily material. The oil was purified by column chromatography on silica gel with a (5 : 1) mixture of AcOEt and hexane to give two fractions; the first fraction contained **5ba** and **6ba**, the second fraction contained **3ba**.

3ba: Yield: 336 mg (64%); Colorless prisms (from a mixture of CH_2Cl_2 and hexane); mp 222.5—223.5 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=8.17 (1H, s), 7.35-6.84 (8H, A_2B_2q, J=8.9 Hz), 7.11-6.78 (8H, A_2B_2q, J=8.9 Hz), 5.42 (1H, s), 3.80 (6H, s), 3.75 (6H, s), 3.45 (2H, m), 3.44 (1H, bs), 3.27 (1H, m), and 2.74 (2H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=160.0, 158.5, 157.9, 133.8, 133.7, 132.6, 130.2, 129.4, 128.0, 113.6, 113.4, 96.5, 77.8, 58.5, 55.2, 55.1, 53.6, 49.3, and 47.7; IR ($CHCl_3$) 3600, 3010, 1730, and 1610 cm^{-1}; MS m/z 616 (M^+). Found: C, 75.79; H, 5.79%. Calcd for $C_{39}H_{36}O_7$: C, 75.96; H, 5.88%.

5ba (16%) and 6ba (7%): Analytical data are shown in Tables 3 and 4.

8,8-Bis(4-methoxyphenyl)-2-[bis(4-methoxyphenyl)methylene]tetracyclo[4.3.0.0^{3,9}.0^{4,7}]nonane-*exo*-5,7-diol (3bb). Several drops of 28% sodium methoxide methanol were added to a solution of **3ba** (100 mg, 0.16 mmol) in methanol (10 ml) and the mixture was stirred for 30 min at room temperature. The reaction mixture was then treated according to the procedure employed for the preparation of **3ab** to give **3bb**. Yield: 94.1 mg (100%); Colorless crystals (from a mixture of CH_2Cl_2 and hexane); mp 221.3—224.3 °C (decomp); ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.34 (4H, d, J=9.0 Hz), 7.06 (4H, d, J=9.0 Hz), 6.82 (4H, d, J=9.0 Hz), 6.79 (4H, d, J=9.0 Hz), 4.58 (1H, d, J=6.0 Hz), 3.98 (1H, s), 3.79 (6H, s), 3.75 (6H, s), 3.70 (2H, dd, J=7.0 and 4.0 Hz), 3.20 (1H, t, J=4.0 Hz), 3.17 (1H, d, J=6.0 Hz), and 2.55 (2H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=158.4, 157.9, 135.6, 134.0, 132.9, 130.1, 129.4,

Table 4. ^{1}H and ^{13}C NMR Spectral Data of **5** and **6**

	^{1}H NMR (270 MHz, $CDCl_3$), δ (ppm)	^{13}C NMR (67.5 MHz, $CDCl_3$), δ (ppm)
5ac	7.41—7.08 (20H, m), 3.20 (2H, m), 2.98 (2H, m), 2.58 (2H, t, J=6.0 Hz), and 2.38 (2H, bs).	143.6, 142.1, 128.2, 128.1, 128.0, 126.2, 125.8, 87.8, 63.8, 51.4, 48.2, and 42.7.
5ba	8.27 (2H, m), 7.23 (4H, d, J=9.0 Hz), 7.13 (4H, d, J=9.0 Hz), 6.78 (4H, d, J=9.0 Hz), 6.74 (4H, d, J=9.0 Hz), 3.77 (6H, s), 3.74 (6H, s), 3.58 (2H, m), 3.23 (2H, t, J=6.0 Hz), and 2.96 (2H, m).	159.3, 158.3, 157.7, 135.2, 133.4, 129.4, 129.0, 113.5, 113.4, 91.8, 64.7, 55.1, 50.6, 48.8, and 43.7.
5bb	7.29 (4H, d, J=9.0 Hz), 7.20 (4H, d, J=9.0 Hz), 6.79 (4H, d, J=9.0 Hz), 6.73 (4H, d, J=9.0 Hz), 3.77 (6H, s), 3.72 (6H, s), 3.13 (2H, m), 2.91 (2H, m), 2.58 (2H, t, J=6.0 Hz), and 2.35 (2H, bs).	157.7, 157.4, 136.2 ,134.7, 129.2, 128.9, 113.5, 113.4, 88.1, 62.5, 55.1, 51.8, 48.4, and 42.6.
5bc	8.27 (1H, s), 7.30 (2H, d, J=9.0 Hz), 7.29 (2H, d, J=9.0 Hz), 7.27 (2H, d, J=9.0 Hz), 7.14 (2H, d, J=9.0 Hz), 6.78 (2H, d, J=9.0 Hz), 6.75 (2H, d, J=9.0 Hz), 6.74 (2H, d, J=9.0 Hz), 6.71 (2H, d, J=9.0 Hz), 3.77 (3H, s), 3.74 (3H, s), 3.73 (3H, s), 3.71 (3H, s), 3.59 (3H, s), 3.45 (2H, m), 3.28 (1H, m), 2.96 (2H, m), and 2.86 (1H, m).	159.4, 158.0, 157.7, 157.5, 157.3, 136.2, 135.2, 134.8, 133.9, 129.5, 129.4, 129.2, 129.0, 113.5, 113.3, 113.2, 113.1, 93.1, 92.6, 64.9, 63.7, 55.1, 55.0, 54.6, 51.7, 50.2, 48.4, 46.3, 42.8, and 42.0.
5ca	8.12 (2H, s), 3.23 (2H, m), 3.17 (2H, m), 2.29 (2H, m), 0.92 (6H, s), and 0.81 (6H, s).	160.1, 92.1, 50.72, 50.66, 47.3, 40.8, 17.8, and 17.4.
5cb	8.13 (1H, s), 3.06 (1H, m), 2.99 (2H, m), 2.80 (1H, m), 2.25 (2H, m), 2.14 (1H, bs), 0.89 (3H, s), 0.87 (3H, s), 0.79 (3H, s), and 0.76 (3H, s).	160.4, 93.0, 87.5, 52.4, 50.4, 50.2, 49.2, 48.1, 46.9, 41.5, 39.0, 17.5, 17.4, 17.3, and 16.9.
5cc[a]	2.74—2.68 (4H, m), 2.23—2.21 (2H, m), 0.84 (6H, s), and 0.74 (6H, s).	88.4, 51.9, 49.0, 47.7, 39.6, 16.95, and 16.91.
6ac	7.39—7.11 (20H, m), 3.75 (2H, quin, J=2.0 Hz), 2.73 (4H, t, J=2.0 Hz), and 2.23 (2H, bs).	141.5, 128.3, 126.2, 88.9, 65.3, 49.8, and 46.8.
6ba	7.90 (2H, s), 7.15 (8H, d, J=9.0 Hz), 6.77 (8H, d, J=9.0 Hz), 3.75 (12H, s), 3.80—3.70 (2H, m), and 3.33 (4H, t, J=2.0 Hz).	160.7, 158.2, 131.8, 129.4, 113.8, 94.1, 65.4, 55.2, 49.6, and 46.4.
6bb	7.27 (8H, d, J=9.0 Hz), 6.78 (8H, d, J=9.0 Hz), 3.74 (12H, s), 3.65 (2H, m), 2.68 (4H, t, J=6.0 Hz), and 2.19 (2H, s).	157.8, 133.9, 129.2, 113.6, 89.0, 64.0, 55.1, 49.9, and 46.8.
6bc	7.85 (1H, s), 7.26 (4H, d, J=9.0 Hz), 7.17 (4H, d, J=9.0 Hz), 6.77 (4H, d, J=9.0 Hz), 6.75 (4H, d, J=9.0 Hz), 3.74 (12H, s), 3.59 (2H, m), 3.40 (3H, s), 3.20 (2H, m), and 3.08 (2H, m).	161.3, 158.1, 157.8, 133.8, 132.5, 129.54, 129.49, 113.7, 113.4, 94.5, 94.3, 65.3, 64.4, 56.1, 55.13, 55.10, 50.7, 49.5, 46.0, and 45.0.
6ca	2.54 (6H, bs) and 1.26 (12H, s).	88.6, 49.3, 49.1, 44.4, and 14.9.

a) ^{1}H NMR (360 MHz, $CDCl_3$), ^{13}C NMR (90 MHz, $CDCl_3$).

126.8, 113.6, 97.4, 75.6, 58.2, 55.2, 55.1, 53.6, 50.8, and 47.3; IR (KBr) 3510, 2960, and 1610 cm^{-1}; MS m/z 588 (M^+). Found: C, 77.24; H, 6.07%. Calcd for $C_{38}H_{36}O_6$: C, 77.53; H, 6.16%.

Reaction of 1b with *p*-TsOH. Preparation of 5,5-Bis(4-methoxyphenyl)-4-[4-bis(4-methoxyphenyl)methylene-2-cyclobutenyl]-2-cyclopenten-1-one (4b). A mixture of **1b** (50 mg, 0.085 mmol) and *p*-TsOH (4.4 mg, 0.0256 mmol) in a (1:1) mixture of water and CH_2Cl_2 (2 ml) was stirred for 48 h at room temperature. The reaction mixture was then poured into saturated aqueous $NaHCO_3$ (10 ml) and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried over $MgSO_4$, and evaporated to give a yellow oil. The oil was purified by preparative thin-layer chromatography on silica gel with a developing solvent of a (4:1) mixture of $CHCl_3$ and AcOEt. The band with an R_f value of 0.7 gave pure **4b**. Yield: 5 mg (10%); Pale yellow oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.55 (1H, dd, J=6.0 and 2.5 Hz), 7.22 (2H, d, J=8.8 Hz), 7.20 (2H, d, J=8.8 Hz), 6.97 (2H, d, J=8.8 Hz), 6.94 (2H, d, J=9.2 Hz), 6.87 (2H, d, J=9.1 Hz), 6.86 (2H, d, J=8.8 Hz), 6.79 (2H, d, J=9.2 Hz), 6.70 (2H, d, J=9.1 Hz), 6.46 (1H, d, J=2.5 Hz), 6.20 (1H, dd, J=6.0 and 2.1 Hz), 5.50 (1H, d, J=2.5 Hz), 3.87 (3H, s), 3.80 (3H, s), 3.77 (3H, s), 3.75 (3H, s), 3.63 (1H, m), and 3.49 (1H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=210.0, 168.3, 159.1, 158.8, 158.3, 158.2, 144.7, 139.0, 137.4, 135.6, 133.9, 132.9, 132.8, 132.5, 131.0, 130.6, 130.3, 129.5, 126.5, 113.9, 113.7, 113.3, 113.2, 62.0, 55.4, 55.3, 55.2, 55. 1, 50.8, and 49.3; IR ($CHCl_3$) 1705 cm^{-1}; MS m/z 570 (M^+). Found: m/z 570.2389. Calcd for $C_{38}H_{34}O_5$: M, 570.2404.

Reaction of 1c with Formic Acid. Preparation of 5,9-Diformyloxy-6,6,10,10-tetramethylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane (5ca), 9-Formyloxy-6,6,10,10-tetramethylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decan-5-ol (5cb), and 6,6,10,10-Tetramethylpentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-5,9-diol (5cc), and 5,5,10,10-Tetramethylpentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]-decane-1,4-diol (6ca). A solution of **1c** (200 mg, 0.91 mmol) in formic acid (20 ml) was stirred for 12 h at room temperature, then poured into ice-water. The resulting mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with 10% $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated to give an oil. Half of the oil was purified by column chromatography on silica gel with a (10:1) mixture of hexane and AcOEt as an eluent to give three fractions; the first fraction contained **5ca**, the second fraction contained **5cb**, and the third fraction contained **5cc**. Compounds **5ca**, **5cb**, and **5cc** were obtained in 60%, 10%, and 7% yields, respectively. In this run D_{2h}-bishomocubanes were not de-

tected. The remainder of the oil was treated with sodium methoxide in methanol at room temperature. A work-up according to the procedure used for the preparation of **3ab** gave **5cc** and **6ca** in 82% and 8% yields, respectively. The analytical data of these compounds are shown in Tables 3 and 4.

Reaction of 1c with *p*-TsOH. Preparation of 5cc and 6ca. A solution of **1c** (50 mg, 0.23 mmol) and *p*-TsOH (12 mg, 0.068 mmol) in a (1:1) mixture of water and CH_2Cl_2 was stirred for 12 h at room temperature, then poured into saturated aqueous $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine and water, dried over $MgSO_4$, and evaporated to give an oily material which was purified by column chromatography on silica gel with a (10:1) mixture of hexane and AcOEt as an eluent to give two fractions: the first fraction contained **5cc** and the second fraction contained **6ca**. Compounds **5cc** and **6ca** were obtained in 80% and 8% yields, respectively. The analytical data of **5cc** and **6ca** are shown in Tables 3 and 4.

Dimethyl Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1, 4-dicarboxylate (7). This compound was prepared according to the procedure described in the literature.[2] Yield: 44%; mp 162.3—164.1 °C (from a mixture of $CHCl_3$ and hexane)(lit, 161—162 °C).

Methyl 4-(Hydroxydiphenylmethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylate (8a). A solution of phenylmagnesium bromide, prepared from bromobenzene (7.13 g, 45.4 mmol) and Mg (1.10 g, 45.4 mmol), in THF (25 ml) was added to a solution of **7** (5.00 g, 22.7 mmol) in THF (25 ml). The mixture was refluxed for 2 h, poured into ice-water at pH 3, and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with 3% NaOH and brine, respectively, and dried over $MgSO_4$. After removal of the CH_2Cl_2, the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **8a**. Recrystallization from $CHCl_3$ gave pure **8a** as colorless fine needles. Yield: 3.79 g (49%); mp 168.0—169.5 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.34—7.23 (10H, m), 4.11—4.01 (6H, m), 3.68 (3H, s), and 2.19 (1H, bs); ^{13}C NMR (90 MHz, $CDCl_3$) δ=172.5, 143.7, 128.1, 127.2, 126.6, 78.4, 64.1, 55.3, 51.4, 45.4, and 45.2; IR ($CHCl_3$) 3590, 3000, and 1720 cm^{-1}; MS *m/z* 344 (M^+). Found: C, 80.01; H, 5.98%. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%.

Methyl 4-[Hydroxybis(4-methoxyphenyl)methyl]-pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylate (8b). This compound was prepared from Mg (2.21 g, 91.0 mmol), 4-bromoanisole (17.0 g, 91.0 mmol), and **7** (10.0 g, 45.5 mmol) in THF (50 ml) according to the procedure employed for the preparation of **8a**. Yield: 9.20 g (50%); Pale yellow oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.15·6.83 (8H, A_2B_2q, *J*=8.9 Hz), 4.08 (3H, m), 4.01 (3H, m), 3.79 (6H, s), 3.69 (3H, s), and 2.08 (1H, bs); ^{13}C NMR (90 MHz, $CDCl_3$) δ=172.5, 158.7, 136.5, 127.8, 113.5, 77.9, 64.5, 55.4, 55.2, 51.5, 45.4, and 45.3; IR ($CHCl_3$) 3600, 3010, 1720, 1615, 1590, and 1520 cm^{-1}; MS *m/z* 404.1631. Calcd for $C_{25}H_{24}O_5$: M, 404.1624.

Methyl 4-(1-Hydroxy-1-methylethyl)pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane-1-carboxylate (8c). This compound was prepared from **7** (10.0 g, 45.5 mmol) and methylmagnesium iodide according to the procedure employed for the preparation of **8a**. Yield: 2.55 g (26%); Colorless crystals (from a mixture of benzene and hexane); mp 68.7—69.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=4.07 (3H, m), 3.88 (3H, m), 3.71 (3H, s), and 1.15 (6H, s); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=172.7, 70.0, 65.2, 56.4, 51.4, 45.1, 43.7, and 22.7; IR ($CHCl_3$) 3600, 2980, and 1720 cm^{-1}; MS *m/z* 220 (M^+). Found: C, 69.16; H, 7.30%. Calcd for $C_{13}H_{16}O_3$·1/4H_2O: C, 69.47; H, 7.40%.

Methyl 1-Formyloxy-9,9-diphenylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate (9aa). Compound **8a** (440 mg, 1.28 mmol) in formic acid (5 ml) was stirred for 1 h at room temperature, poured into ice-water (100 ml), and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated to give an oil. The oil was purified by column chromatography on silica gel with $CHCl_3$ to give two fractions. The first fraction contained **9aa**: Yield: 231 mg (49%); Colorless crystals (from AcOEt); mp 216.3—218.3 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=8.24 (1H, s), 7.32—7.14 (10H, m), 3.92—3.87 (2H, m), 3.71—3.66 (2H, m), 3.67 (3H, s), and 3.57—3.52 (2H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=172.3, 159.2, 139.7, 128.4, 128.1, 126.6, 94.8, 70.2, 51.5, 48.0, 46.8, 46.1, 44.5, and 43.3; IR (KBr) 3000 and 1715 cm^{-1}; MS *m/z* 372 (M^+). Found: C, 77.19; H, 5.32%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%. The second fraction contained **methyl 1-hydroxy-9,9-diphenylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate**: Yield: 198 mg (45%); Colorless crystals (from AcOEt); mp 195.1—195.9 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ=7.37—7.15 (10H, m), 3.89 (1H, t, *J*=5.0 Hz), 3.68 (3H, s), 3.63 (3H, m), 3.25 (2H, m), and 2.27 (1H, s); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=172.7, 140.5, 128.3, 128.1, 126.4, 91.3, 67.6, 51.5, 49.5, 47.7, 46.3, 44.3, and 41.1; IR (KBr) 3420, 2980, and 1690 cm^{-1}; MS *m/z* 344 (M^+). Found: C, 79.99; H, 5.81%. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%.

Methyl 1-Formyloxy-9,9-bis(4-methoxyphenyl)-pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate (9ba). Compound **8b** (2.02 g, 5.00 mmol) in formic acid (10 ml) was stirred for 1 h at room temperature. The reaction mixture was then treated according to the procedure employed for the preparation of **9aa** to give **9ba**. Yield: 2.16 g (100%); ^{1}H NMR (360 MHz, $CDCl_3$) δ=8.25 (1H, s), 7.19·6.77 (8H, A_2B_2q, *J*=8.9 Hz), 3.89 (1H, m), 3.81 (1H, m), 3.76 (6H, m), 3.68 (3H, s), 3.66 (2H, m), and 3.52 (2H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ=172.5, 159.3, 158.2, 132.1, 129.4, 113.5, 95.3, 69.1, 55.1, 51.5, 48.3, 46.9, 46.2, 44.6, and 43.2; IR ($CHCl_3$) 3000, 2950, 2840, 1725, 1610, 1510, 1465, and 1440 cm^{-1}; MS *m/z* 432 (M^+). Compound **9ba** was used for the following step without purification.

Methyl 1-Methoxy-9,9-bis(4-methoxyphenyl)-pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate (9bb). A mixture of **8b** (500 mg, 1.24 mmol) and *p*-TsOH (64 mg, 0.371 mmol) in MeOH (40 ml) was stirred at room temperature until **8b** disappeared on TLC, then poured into ice-water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated to give an oily material. The oil was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give pure **9bb**. Yield: 359 mg (69%); Oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ=7.28·6.75 (8H, A_2B_2q, *J*=8.6 Hz), 3.80 (1H, t, *J*=5.0 Hz), 3.73 (6H, s), 3.67 (3H, s), 3.65 (2H, m), 3.56 (3H, s), and 3.53 (3H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ=172.7, 157.7, 133.2, 129.5, 113.2, 97.3, 67.6, 55.1, 55.0, 51.4, 49.5, 47.7, 44.2,

and 41.9; IR ($CHCl_3$) 2980, 1720, and 1605 cm^{-1}. Found: m/z 418.1793. Calcd for $C_{26}H_{26}O_5$: 418.1781.

Methyl 1-Formyloxy-9,9-dimethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate (9ca). A mixture of **8c** (500 mg, 2.27 mmol) and formic acid (20 ml) was stirred for 12 h at room temperature. Treatment of the reaction mixture according to the procedure employed for the preparation of **9aa** gave an oily material, which was purified by column chromatography on silica gel with a (50:1) mixture of $CHCl_3$ and methanol to give two fractions. The first fraction contained **9ca**: Yield: 16%; Oil; ^1H NMR (360 MHz, $CDCl_3$) δ=8.15 (1H, s), 3.76 (1H, m), 3.68 (3H, s), 3.61 (2H, m), 3.44 (2H, m), 2.80 (1H, t, J=5.0 Hz), and 0.80 (6H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ=172.8, 159.9, 95.1, 54.6, 51.4, 47.8, 46.8, 44.6, 44.2, 42.0, and 14.0; IR ($CHCl_3$) 2950, 1735, and 1720 cm^{-1}; MS m/z 248 (M^+). Found: C, 67.60; H, 6.34%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%. The second fraction contained **methyl 1-hydroxy-9,9-dimethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-4-carboxylate**: Yield: 56%; Oil; ^1H NMR (360 MHz, $CDCl_3$) δ=3.67 (3H, s), 3.56 (2H, m), 3.52 (1H, m), 3.19 (2H, m), 2.79 (1H, t, J=5.0 Hz), 1.84 (1H, s), and 0.74 (6H, s); ^{13}C NMR (90 MHz, $CDCl_3$) δ=173.1, 91.6, 52.5, 51.4, 49.8, 47.5, 45.0, 43.9, 40.3, and 13.5; IR ($CHCl_3$) 3590, 3450, 2950, and 1720 cm^{-1}; MS m/z 220 (M^+). Found: m/z 220.1092. Calcd for $C_{13}H_{16}O_3$: M, 220.1099.

Ozonolysis of 3aa and 3ba. Ozone gas was bubbled through a solution of **3aa** (42 mg, 0.085 mmol) in CH_2Cl_2 at −78 °C for 20 min. (The reaction was followed by TLC). After **3aa** had disappeared, an excess of dimethyl sulfide was added. The resulting mixture was stirred for 1 h at room temperature and concentrated in order to remove the residual dimethyl sulfide. The residue was dissolved in CH_2Cl_2, then washed with brine, dried over $MgSO_4$, and evaporated to give a solid mass. The solid was purified by preparative thin-layer chromatography with $CHCl_3$ as a developing solvent to give pure benzophenone in a 60% yield.

Compound **3ba** gave 4,4′-dimethoxybenzophenone in a 54% yield according to the procedure used for the ozonolysis of **3aa**.

Ozonolysis of 4a and 4b. Ozone gas was bubbled through a solution of **4a** (50 mg, 0.11 mmol) in CH_2Cl_2 (10 ml) at −15 °C. The reaction mixture was treated according to the procedure used for the ozonolysis of **3aa** to give benzophenone in a 60% yield.

Compound **4b** was treated according to the procedure used for the ozonolysis of **4a** to give 4,4′-dimethoxybenzophenone in a 60% yield.

Rearrangement Reactions. Reaction of 1 and 2 under a Variety of Acidic Conditions. Two typical examples are given to illustrate the general procedure.

1. A solution of **1** (1.5 mmol) in formic acid (25 ml) was stirred at room temperature, then poured into ice-water and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated to give an oily material. The oil was treated in methanol containing several drops of 28% sodium methoxide methanol solution at room temperature for 30 min and then neutralized with 1 M HCl. After removal of the methanol, the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried over $MgSO_4$, and evaporated to give an oily material or a solid mass. Separation and purification of the components by a combination of column and preparative thin-layer chromatographies on silica gel with a suitable solvent gave analytically pure products (**3ab**, **3bb**, **4**, **5ac**, **5bb**, **5cc**, **6ac**, **6bb**, and **6ca**).

2. A mixture of **1** (1.0 mmol) and *p*-TsOH (0.30 mmol) in a (1:1) mixture of water and CH_2Cl_2 (3 ml) was stirred at room temperature. The reaction mixture was poured into saturated aqueous $NaHCO_3$ (10 ml) and extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with brine, dried over $MgSO_4$, and evaporated to give oily materials. The oils were purified by a combination of column and preparative thin-layer chromatographies on silica gel with a suitable solvent to give analytically pure **4**. The results are summarized in Tables 1 and 2.

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6) T. Hasegawa, Ph. D. Dissertation, Osaka University, Osaka, Japan, 1993. Reaction of **1** with formic acid gives two types of a free carbocation intermediate (**E**) and an ion-pair intermediate (**F**) (Chart 4). **E** reacts preferentially with an external nucleophile ($^-$OCHO). **F** reacts concertedly with either an internal ($^-$OH) nucleophile or an external ($^-$OCHO) nucleophile. When R is a methyl group, **F** is formed to react preferentially with $^-$OH. When R is a 4-methoxyphenyl group, **E** is formed to react selectively with $^-$OCHO. When R is a phenyl group, both intermediates (**E** and **F**) are formed to react with both nucleophiles ($^-$OH and $^-$OCHO).

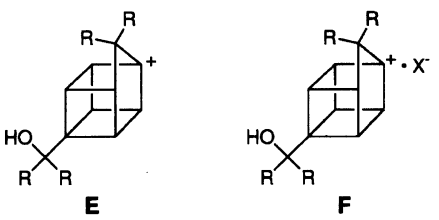

Chart 4.

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