Photochemical Chlorocarbonylation of HCTD by Oxalyl Chloride. Carbocation-Mediated Rearrangement of HCTD Derivatives to Novel, Substituted Heptacyclopentadecanes

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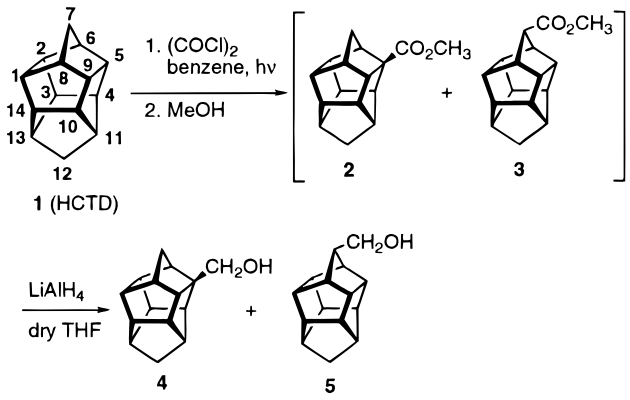
Photochemical chlorocarbonylation of heptacyclo[6.6.0.0.^{2,6}0.^{3,13}0.^{4,11}0^{5,9}.0^{10,14}]tetradecane ("HCTD", **1**), performed by irradiating a solution of oxalyl chloride and **1** in benzene, followed by reaction of the crude reaction product with methanol, afforded a mixture of methyl 1- and 7-(HCTD)carboxylates (i.e., **2** and **3**, product ratio **2**/**3** = 3:1). Reduction of the mixture of cage esters thereby obtained with $LiAlH_4$ afforded the corresponding cage alcohols (**4** and **5**, respectively), which could be separated via column chromatographic methods. Subsequently, **4** and **5** were converted into the corresponding cage tosylates (i.e., **7** and **13**, respectively). Reaction of **7** with $CF_3CO_2H-CHCl_3$ resulted in solvolysis with concomitant skeletal rearrangement, thereby affording **8a**. The corresponding reaction performed by starting with cage tosylate **13** also resulted in solvolysis with accompanying skeletal rearrangement, thereby affording **18a**.

Introduction

Heptacyclo[6.6.0.0.^{2,6}0.^{3,13}0.^{4,11}0^{5,9}.0^{10,14}]tetradecane("HCTD", **1**, Scheme 1) was first prepared via iron carbonyl promoted cyclodimerization of norbornadiene.[1] This unusual hydrocarbon possesses a highly rigid polycarbocyclic structure with D_{2d} point symmetry. As a complex "cyclooctaquinane",[2] HCTD can be regarded as being a repository of five-membered carbocyclic rings. However, the potential value of compounds of this type as intermediates in polyquinane synthesis remains to be systematically explored.

Although HCTD remained a laboratory curiosity for more than a decade after it was first synthesized, the 1970s witnessed renewed interest in the HCTD ring system that continues to the present day.[2] Thus, 7-monosubstituted- and 7,12-disubstituted-HCTDs have been synthesized readily via transition metal promoted [4 + 4] cyclodimerization of 7-substituted norbornadienes[1,3,4] and via direct oxidative functionalization of HCTD with Gif-type reagents.[5] However, application of more vigorous oxidative methods frequently results in cleavage of the C(1)−C(2) σ-bond in **1** with concomitant formation of C(10)- and C(14)-functionalized hexacyclo-[6.6.0.0.^{2,6}0.^{3,13}0^{4,11}.0^{5,9}]tetradecanes.[6,7] We now report the results of photochemical chlorocarbonylation of HCTD by using oxalyl chloride[8] and some interesting and synthetically useful transformations of the resulting 1- and 7-functionalized HCTDs.

Scheme 1



Photochemical Chlorocarbonylation of HCTD. Photolysis of a benzene solution of HCTD in the presence of excess oxalyl chloride in benzene solution[8] followed by reaction of the mixture of acid chlorides thereby obtained with MeOH afforded a mixture of methyl 1- and 7-(HCTD)carboxylates (i.e., **2** and **3**, product ratio **2**/**3** = 3:1; Scheme 1) in 53% combined yield. Despite our best efforts, this mixture could not be separated via column chromatography. Instead, the mixture of esters was subjected to $LiAlH_4$ promoted reduction; a mixture of the corresponding alcohols [i.e., 1- and 7-hydroxymethyl-(HCTD), **4** and **5**, respectively] was thereby obtained.

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(2) Chow, T. J. *Proc. Natl. Sci. Counc., Repub. China, Part A* **1992**, *16*, 89.

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(6) (a) Chow, T. J.; Wu, T.-K. *J. Org. Chem.* **1988**, *53*, 1102. (b) Chow, T. J.; Feng, J.-J.; Shih, H.-J.; Wu, T.-K.; Tseng, L.-H.; Wang, C.-Y.; Yu, C. *J. Chin. Chem. Soc.* **1988**, *35*, 291. (c) Chow, T. J.; Wu, T.-K. *J. Org. Chem.* **1991**, *56*, 6833.

(7) One important exception to this statement is provided by the reaction of HCTD with $Pb(OAc)_4-CF_3CO_2H$, which affords 1-hydroxy-(HCTD) as the major reaction product.[6a]

(8) (a) For a review, see: Bashir-Hashemi, A.; Doyle, G. *Aldrichim. Acta* **1996**, *29*, 43. (b) Bashir-Hashemi, A.; Li, J.; Gelber, N.; Ammon, H. *J. Org. Chem.* **1995**, *60*, 698. (c) Bashir-Hashemi, A.; Li, J.; Gelber, N. *Tetrahedron Lett.* **1995**, *36*, 1233.

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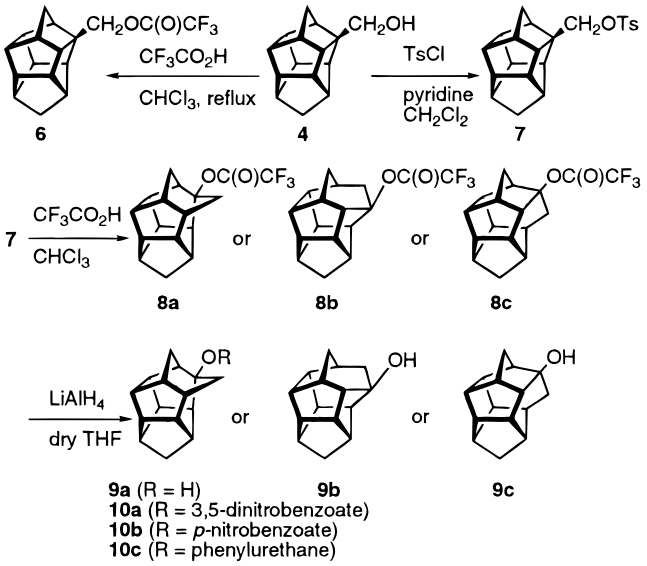
Scheme 2



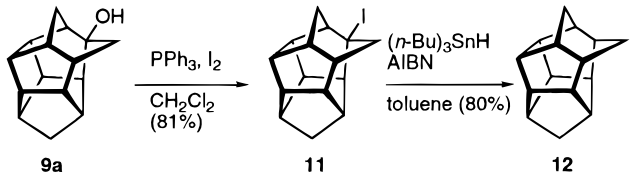
This mixture of cage alcohols could be separated readily via column chromatography. In this way, isomerically pure **4** and **5** were obtained in 62% and 21% yield, respectively.

Reaction of 1-Hydroxymethyl(HCTD) (4) with $CF_3CO_2H-CHCl_3$. A $CHCl_3$ solution of **4** that contained excess trifluoroacetic acid (TFAA) was refluxed for 1.5 h, thereby affording single product (cage trifluoroacetate ester) in essentially quantitative yield. The ^{13}C NMR spectrum of this product displays a resonance signal at δ 71.4 (t), which most likely can be assigned to a $CH_2-O(CO)CF_3$ moiety in the product. This result suggests that reaction of **4** with TFAA under these conditions results in simple esterification of the OH group in **4** without concommitant skeletal rearrangement, thereby affording **6** (Scheme 2). This suggestion was confirmed by the fact that subsequent $LiAlH_4$ promoted reduction of the esterification product (**6**) indeed resulted in its smooth conversion to starting material (**4**) in 90% isolated yield.

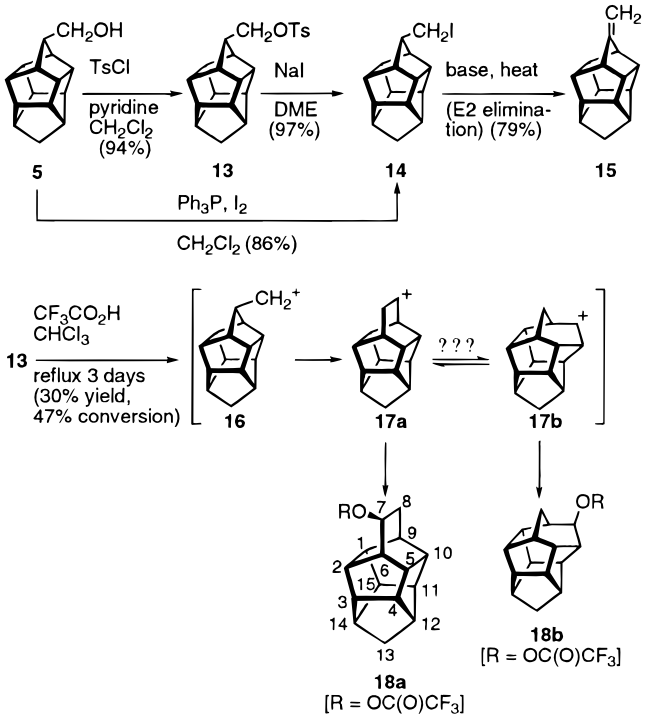
Acid-Promoted Rearrangement of 1-(*p*-Toluenesulfonyloxymethyl)(HCTD) (7). Cage tosylate **7** rearranged smoothly when allowed to react with TFAA-$CHCl_3$ at ambient temperature. As indicated in Scheme 2, any (or all) of three cage trifluoroacetates (i.e., **8a**−**c**) presumably could be formed via carbocation mediated Wagner−Meerwein rearrangement in this system. However, in our hands, a single product was obtained as a viscous oil (81% yield). In addition, it is worthwhile to note that this same rearranged trifluoroacetate was obtained in 81−89% yield when a solution of **7** in CH_2Cl_2−hexane was stirred with silica gel at ambient temperature for 24 h.

Lithium aluminum hydride promoted reduction of the product thereby obtained afforded the corresponding alcohol (**9a**, **9b**, or **9c**) in 92% yield. In an effort to obtain a crystalline derivative of this alcohol, it was converted sequentially into the corresponding 3,5-dinitrobenzoate, *p*-nitrobenzoate, and phenylurethane. However, we were unable to obtain a single crystal of any of these solid derivatives that proved to be suitable for X-ray structural analysis. Accordingly, a chemical method to establish the structure of this alcohol, **9**, was sought.

Scheme 3



Scheme 4



The method that was employed for this purpose and that ultimately proved to be successful is shown in Scheme 3. Reaction of a CH_2Cl_2 solution of alcohol **9** with Ph_3P, I_2 reagent[9] proceeded smoothly to afford the corresponding cage iodide, **11** (81% yield). Subsequent reductive dehalogenation of **11** produced the corresponding cage hydrocarbon, **12** (80% yield, Scheme 3).

The proton noise-decoupled ^{13}C NMR spectrum of the hydrocarbon, **12**, thereby obtained contains 10 resonance signals; this observation suggests that **12** possesses a 2-fold symmetry element. It should be noted that any of three isomeric $C_{15}H_{18}$ hydrocarbons could have resulted via the two-step reaction sequence shown in Scheme 3 (i.e., depending on whether the starting alcohol possesses structure **9a**, **9b**, or **9c**). However, only one of these $C_{15}H_{18}$ hydrocarbons, i.e. **12**, possesses a 2-fold symmetry element as required by the ^{13}C NMR spectral evidence cited above. Based upon this observation, we assign structure **9a** to the alcohol formed via reaction of **7** with TFAA−$CHCl_3$ followed by $LiAlH_4$ promoted reduction of the resulting rearranged cage trifluoroacetate (i.e., **8a**).

Acid-Promoted Rearrangement of 7-(*p*-Toluenesulfonyloxymethyl)(HCTD) (13). 7-Hydroxymethyl-(HCTD) (i.e., **5**) was converted into the corresponding tosylate derivative, **13**, by using the method shown in Scheme 4. The fact that this reaction proceeded without concomitant rearrangement was demonstrated via sub-

(9) (a) Wiley: G. A.; Hershkowitz, R. L.; Rein, R. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964. (b) Verheyden, J. P. H.; Moffatt, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2093.

sequent conversion of **13** into 7-methylene(HCTD)[3c] (i.e., **15**) by using the method shown in Scheme 4.

Cage tosylate **13** proved to be considerably more resistant to solvolysis in TFAA−$CHCl_3$ than was observed to be the case for the corresponding solvolysis of **7**. Thus, it was necessary to reflux a $CHCl_3$ solution of **13** with TFAA−$CHCl_3$ for 3 days in order to complete the reaction.

Analysis of the ^1H and ^{13}C NMR spectra of the reaction product clearly indicated that solvolysis of **13** had proceeded with accompanying skeletal rearrangement. Thus, inspection of the off-resonance decoupled ^{13}C NMR spectrum of the solvolysis product thereby obtained revealed the presence of two triplet resonance signals at δ 27.7 and 41.8. In addition, inspection of proton noise decoupled ^{13}C NMR spectrum of this product reveals that its structure does not possess any element of symmetry.

Assignment of the structure of the rearranged product formed via solvolysis of **13** was made via analysis of its 2-D $^1H-^1H$ COSY NMR spectrum. Thus, we observe a clear correlation between the *H*C(7)−OC(O)CF_3 proton at δ 5.21 and the protons situated on C(8) that comprise the AB pattern associated with the adjacent methylene group (absorptions centered at δ 1.55 and 2.18). In addition, there is clear evidence for coupling between *H*C(7)−OC(O)CF_3 (δ 5.21) and the adjacent bridgehead proton situated at C(9) (resonance signals located at ca. δ 2.2). Based upon these observations, we assign structure **18a** (Scheme 4) to the rearranged product formed via solvolysis of **13**.

Results of Theoretical Calculations of Relative Stabilities of Carbocationic Intermediates Associated with Solvolysis−Rearrangement of 7 and 13. The relative stabilities of three potential carbocationic precursors to **8a**−**8c** (i.e., **20a**−**20c**, respectively) and also of two potential carbocationic precursors to **18a** and **18b** (i.e., **17a** and **17b**, respectively) have been calculated by using semiempirical (AM1 Hamiltonian)[10a] and ab initio[10b] computational methods. The results thereby obtained are shown in Table 1.

Inspection of the data in Table 1 reveals a clear thermodynamic preference for the formation of carbocation **20a** via rearrangement of **19**. This result leads to the prediction that carbocation mediated rearrangement of **7** in acidic medium should afford **8a** as the major (or perhaps even exclusive) reaction product.

Interestingly, the results of the corresponding calculations performed for solvolysis rearrangement of **13**, also shown in Table 1, indicate that there may be a slight thermodynamic preference for further Wagner−Meerwein rearrangement of **17a** to **17b**. However, based upon our analysis of the 2-D $^1H-^1H$ COSY NMR spectrum of the product formed via solvolysis−rearrangement of **13** (*vide supra*), we conclude that this expectation is not borne out by experiment.

Summary and Conclusions. Direct functionalization of the HCTD skeleton has been performed in a synthetically useful manner via its facile photochemical chlorocarbonylation by using oxalyl chloride. Methanolic workup of the crude reaction product afforded an intractable mixture of methyl 1- and 7-(HCTD)carboxylates.

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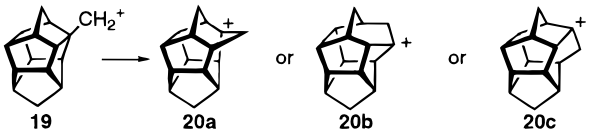
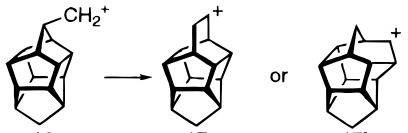
Table 1. Calculated Relative Stabilities of Carbocationic Intermediates (kcal mol^{-1})



19 20a 20b 20c

Method	Relative Energies (kcal-mol^{-1})		
AM1	0.0	3.2	12.8
HF/6-31G*	0.0	2.1	2.9
MP2/6-31G*// HF/6-31G*	0.0	0.8	2.5



16 17a 17b

Method	Relative Energies (kcal-mol^{-1})	
AM1	0.0	2.6
HF/6-31G*	0.9	0.0
MP2/6-31G*// HF/6-31G*	4.0	0.0

(i.e., **2** and **3**, respectively). Lithium aluminum hydride promoted reduction of this mixture of cage esters afforded the corresponding alcohols (i.e., **4** and **5**, respectively), which could be separated via column chromatography. Reaction of cage tosylate **7** (derived from **4**) with TFAA−$CHCl_3$ resulted in solvolysis with concomitant Wagner−Meerwein rearrangement, thereby affording **8a**. Lithium aluminum hydride promoted reduction of **8a** gave **9a**, which subsequently was converted into the corresponding hydrocarbon, **12**. Inspection of the ^{13}C NMR spectrum of **12** reveals that this compound contains a 2-fold symmetry element, and this fact permitted us to assign the structures of **12** and its precursors (**8a**, **9a**, and **11**).

The results of semiempirical and ab initio calculations of the relative stabilities of the three potential carbocationic precursors to **8a**−**8c** (i.e., **20a**−**20c**, respectively, Table 1) are consistent with our conclusion that carbocation mediated solvolysis of **7** should afford principally (or possibly exclusively) **8a**. Finally, reaction of cage tosylate **13** (derived from **5**) with TFAA−$CHCl_3$ also resulted in solvolysis with accompanying skeletal rearrangement, thereby affording **18a**. The structure of this rearranged product was arrived at via analysis of its 2-D $^1H-^1H$ COSY NMR spectrum.

Experimental Section

Melting points are uncorrected. Elemental microanalyses were performed by personnel at M-H-W Laboratories (Phoenix, AZ).

Photochemical Reaction of 1 with Oxalyl Chloride. Method A. A solution of **1** (350 mg, 1.9 mmol) and oxalyl chloride (4 mL, 38 mmol, excess) in dry benzene (100 mL) at ambient temperature was purged with argon during 0.5 h, and the resulting solution was irradiated by using a Hanovia 450 W medium-pressure Hg lamp (Pyrex filter) at ambient temperature during 9 h. The reaction mixture then was concentrated in vacuo, and dry MeOH (40 mL) was added to the residue. The resulting mixture was stirred at ambient tem-

perature for 3 h and was then concentrated *in vacuo*. The oily residue was dissolved in EtOAc (50 mL), and the resulting solution was washed sequentially with 5% aqueous Na_2CO_3 (50 mL) and brine (20 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by using a 0−5% EtOAc−hexane gradient elution scheme.

The first chromatography fraction was concentrated in vacuo to afford recovered **1** (88 mg, 25%). Continued elution of the chromatography column afforded a second fraction which contained a mixture of **2** and **3** (245 mg, 53%; product ratio **2**/**3** = 3:1, as determined by careful integration of the ^{1}H NMR spectrum of the product mixture). Despite several attempts, this mixture could not be separated via column chromatography on silica gel; IR (KBr) 2943 (s), 1726 cm^{-1} (s). Compound **2** data: ^{1}H NMR ($CDCl_3$) δ 1.73−1.80 (m, 3 H), 1.97 (*A*B, J_{AB} = 10.6, Hz, 1 H), 2.38−2.75 (m, 11 H), 3.51 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 42.3 (t), 42.4 (t), 50.8 (d), 51.0 (d), 51.1 (d), 51.5 (d), 51.9 (d), 52.9 (d), 53.1 (d), 53.14 (d), 53.6 (d), 54.5 (d), 57.8 (d), 58.9 (q), 68.5 (s), 177.1 (s). Compound **3** data: ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 2 H), 2.38−2.55 (m, 12 H), 3.06 (s, 1 H), 3.59 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 43.1 (t), 50.3 (d), 51.1 (d), 51.2 (d), 51.8 (d), 52.3 (d), 52.8 (d), 53.1 (d), 59.2 (d), 173.9 (s). Anal. Calcd for $C_{16}H_{18}O_2$ (mixture of **2** and **3**): C, 79.31; H, 7.49. Found: C, 79.39; H, 7.29. This mixture of **2** and **3** was used as obtained in the next step.

$LiAlH_4$-Promoted Reduction of a Mixture of 2 and 3. A suspension of $LiAlH_4$ (85 mg, 2.1 mmol) in dry THF (1.5 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled suspension was added dropwise with stirring a solution of a mixture **2** and **3** (*vide supra*, 130 mg, 0.54 mmol) in dry THF (3 mL) during 10 min. After all of the reagents had been added, the resulting suspension was stirred at 0 °C for 15 min, at which time the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture then was stirred at ambient temperature for 2 h. The reaction mixture was quenched via careful, sequential addition of EtOAc (2 mL) and saturated aqueous NH_4Cl (5 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc−hexane. The first chromatography fraction was concentrated *in vacuo*, thereby affording 1-(hydroxymethyl)heptacyclo-[6.6.0.0.^{2,6}0.^{3,13}0.^{4,11}0^{5,9}.0^{10,14}]tetradecane (**4**, 72 mg, 62%) as a colorless microcrystalline solid. Recrystallization of this material from CH_2Cl_2−hexane produced analytically pure **4** as a colorless microcrystalline solid; mp 136−137 °C; IR (KBr) 3309 (m), 2943 (s), 2874 (m), 1030 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 1 H), 1.69−1.81 (m, 4 H), 1.97 (br s, 1 H), 2.28−2.52 (m, 10 H), 3.38 (*A*B, J_{AB} = 10.8 Hz, 1 H), 3.48 (A*B*, J_{AB} = 10.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 41.1 (t), 42.8 (t), 49.8 (d), 51.1(d, 2 C), 51.5 (d, 2 C), 53.0 (d), 53.1 (d), 53.2 (d), 53.4 (d), 54.9 (d), 55.8 (d), 65.9 (s), 66.3 (t). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.22; H, 8.23.

Continued elution of the chromatography column afforded a second fraction from which 7-(hydroxymethyl)heptacyclo-[6.6.0.0.^{2,6}0.^{3,13}0.^{4,11}0^{5,9}.0^{10,14}]tetradecane (**5**, 24 mg, 21%) was isolated as a colorless viscous oil that slowly solidified upon standing at ambient temperature. Recrystallization of this material from CH_2Cl_2−hexane afforded analytically pure **5** as a colorless microcrystalline solid; mp 81−82 °C; IR (KBr) 3340 (m), 2941 (s), 2864 (m), 1051 cm^{-1} (w); ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 1 H, OH), 1.80 (s, 2 H), 2.30−2.50 (m, 13 H), 3.54 (d, J = 7.52 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 43.0 (t), 50.2 (d), 50.9 (d), 51.1 (d), 52.1 (d), 52.3 (d), 53.0 (d), 53.3 (d), 59.2 (d), 64.0 (t). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.84; H, 8.31.

Method B. A solution of **1** (1.17 g, 6.35 mmol) and oxalyl chloride (6 mL) in dry benzene (180 mL) was purged with argon during 0.5 h, and the resulting solution was irradiated with a Hanovia 450 W medium-pressure Hg lamp (Pyrex filter) at ambient temperature for 11 h. The reaction mixture was concentrated *in vacuo*, and dry MeOH (100 mL) was added to the residue. The resulting mixture was stirred at ambient temperature for 3 h and was then concentrated *in vacuo*. The oily residue was dissolved in EtOAc (100 mL), and the resulting solution was washed sequentially with 5% aqueous Na_2CO_3 (80 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was dissolved in dry THF (10 mL) and then was added dropwise under argon to a cooled (0 °C) suspension of $LiAlH_4$ (631 mg, 15.8 mmol) in dry THF (5 mL) during 0.5 h. After the addition of reagents had been completed, the resulting suspension was stirred at 0 °C for 15 min, at which time the external cold bath was removed. The reaction mixture was allowed to warm gradually to ambient temperature and then was stirred at ambient temperature for 6 h. The reaction mixture was quenched via careful sequential addition of EtOAc (10 mL) and saturated aqueous NH_4Cl (15 mL). The resulting aqueous suspension was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by using a 0−5% EtOAc−hexane gradient elution scheme.

The first chromatography fraction was concentrated *in vacuo*, thereby affording recovered **1** (99 mg, 8%). Continued elution of the chromatography column afforded a second fraction; workup of the second chromatography fraction afforded **4** (643 mg, 47%). The IR, ^{1}H, and ^{13}C NMR spectra of this material are identical in all respects with the corresponding spectra obtained previously for authentic **4** (*vide supra*).

Continued elution of the chromatography column afforded a third fraction, which, when concentrated *in vacuo*, afforded pure **5** (207 mg, 15%). The IR, ^{1}H, and ^{13}C NMR spectra of this material are identical in all respects with the corresponding spectra obtained previously for authentic **5** (*vide supra*).

Reaction of 4 with CF_3CO_2H−$CHCl_3$. To a solution of **4** (80 mg, 0.37 mmol) in $CHCl_3$ (4 mL) was added CF_3CO_2H (0.8 mL, excess) at ambient temperature, and the resulting mixture was refluxed for 1.5 h. At that time, TLC analysis of the reaction mixture revealed the absence of **4**. The reaction mixture was allowed to cool gradually to ambient temperature and then quenched via addition of saturated aqueous $NaHCO_3$ (5 mL). Water (5 mL) was added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Pure **6** (110 mg, 96%) was thereby obtained as colorless viscous oil; IR (film) 2960 (vs), 2881 (s), 1788 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 1.72−1.87 (m, 4 H), 2.11 (br s, 1 H), 2.35 (br s, 2 H) 2.40−2.58 (m, 8 H), 4.17 (AB, J_{AB} = 10.7 Hz, 1 H), 4.27 (AB, J_{AB} = 10.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 41.2 (t), 42.8 (t), 49.8 (d), 51.1 (d), 51.2 (d), 51.6 (d), 52.3 (d), 52.9 (d), 53.1 (d), 53.4 (d, 2 C), 55.8 (d), 56.2 (d), 63.2 (s), 71.4 (t), 114.6 (q, $^1J_{CF}$ = 284.3 Hz), 157.2 (q, $^2J_{CF}$ = 41.6 Hz). Anal. Calcd for $C_{17}H_{17}F_3O_2$: C, 65.80; H, 5.52. Found: C, 66.03; H, 5.74.

1-Hydroxymethylheptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (4). A suspension of $LiAlH_4$ (65 mg, 1.58 mmol) in dry THF (1.0 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled suspension was added dropwise with stirring a solution of **6** (130 mg, 0.54 mmol) in dry THF (2 mL) during 10 min. After all of the ester had been added, the resulting suspension was stirred at 0 °C for an additional 15 min. The external cold bath then was removed, and the reaction mixture was allowed to warm gradually with stirring to ambient temperature during 2 h. The reaction was quenched via addition of EtOAc (1 mL). Saturated aqueous NH_4Cl (5 mL) was added to the quenched reaction mixture, and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 20% EtOAc−

hexane. Pure **4** (62 mg, 90%) was thereby obtained as a colorless microcrystalline solid; mp 136−137 °C. The IR, ^{1}H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **4** (*vide supra*).

1-(*p*-Tosyloxymethyl)heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (7). A solution of *p*-TsCl (389 mg, 2.04 mmol) in dry pyridine (3 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise a solution of **4** (292 mg, 1.36 mmol) in dry CH_2Cl_2 (5 mL) during 15 min. The external ice−water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature while stirring overnight. The reaction mixture was poured into ice−water (50 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (50 mL). The organic layer was washed with ice-cold 5 M aqueous HCl (2 × 10 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by using a 30−100% CH_2Cl_2−hexane gradient elution scheme.

Workup of the first chromatography fraction afforded pure **7** (311 mg, 62%) as a colorless viscous oil which slowly solidified upon standing at ambient temperature. Recrystallization of this material from Et_2O−hexane afforded analytically pure **7** as a colorless microcrystalline solid: mp 73−74 °C; IR (film) 2943 (s), 2864 (m), 1608 (m), 968 (s), 829 (m), 680 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.80−1.78 (m, 4 H), 1.99 (br s, 1 H), 2.23 (br s, 2 H), 2.34−2.48 (m, 11 H), 3.80 (*A*B, J_{AB} = 9.4 Hz, 1 H), 3.87 (A*B*, J_{AB} = 9.4 Hz, 1 H), 7.31 (*AB*, J_{AB} = 8.1 Hz, 2 H), 7.76 (A*B*, J_{AB} = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 41.1 (t), 42.7 (t), 49.7 (d), 51.07 (d), 51.13 (d), 51.5 (d), 52.0 (d), 52.9 (d), 53.0 (d), 53.3 (2 C, d), 55.4 (d), 56.1 (d), 63.2 (s), 73.5 (t), 127.8 (d), 129.7 (d), 133.2 (s), 144.5 (s). Anal. Calcd for $C_{22}H_{24}O_3S$: C, 71.71; H, 6.56. Found: C, 71.92; H, 6.57.

Continued elution of the chromatography column afforded a second fraction; workup of this fraction afforded pure **9a** (59 mg, 20%) as a colorless microcrystalline solid. Recrystallization of this material from Et_2O−hexane produced analytically pure **9a** as a colorless microcrystalline solid; mp 290−291 °C (dec) (sealed tube). The IR, ^{1}H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **9a** (*vide infra*).

Acid-Promoted Rearrangement of 7. To a solution of **7** (99 mg, 0.27 mmol) in $CHCl_3$ (2 mL) was added CF_3CO_2H (TFAA, 0.5 mL, excess) at ambient temperature, and the resulting mixture was stirred at ambient temperature during 1 h. At that time, TLC analysis of the reaction mixture revealed the absence of **7**. The reaction mixture was quenched via addition of saturated aqueous $NaHCO_3$ (5 mL). To the resulting mixture was added water (5 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Pure 3-trifluoroacetoxyheptacyclo[7.6.0.0.^{2,7}0.^{3,14}0.^{5,12}0.^{6,10}0^{11,15}]-pentadecane (**8a**, 135 mg, 81%, one isomer only) was thereby obtained as colorless viscous oil; IR (film) 2964 (vs), 2880 (m), 1788 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 1.54 [t(*AB*), J_{AB} = 12.5, 3.6 Hz, 1 H], 1.64 (t, J = 1.4 Hz, 2 H), 1.70 (d, J = 2.9 Hz, 2 H), 2.06 (A*B*, J_{AB} = 12.5 Hz, 1 H), 2.21 (t, J = 4.1 Hz, 1 H), 2.30−2.90 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 25.7 (t), 33.8 (d), 33.9 (t), 38.8 (d), 42.1 (t), 48.1 (d), 49.0 (d), 49.4 (d), 51.1 (d), 53.7 (d), 54.7 (d), 55.0 (d), 55.7 (d), 56.3 (d), 95.6 (s), 114.5 (q, $^1J_{CF}$ = 285.2 Hz), 157.2 (q, $^2J_{CF}$ = 40.8 Hz). Anal. Calcd for $C_{17}H_{17}F_3O_2$: C, 65.80; H, 5.52. Found: C, 65.59; H, 5.27.

Heptacyclo[7.6.0.0^{2,7}.0^{3,14}.0^{5,12}.0^{6,10}.0^{11,15}]pentadecan-3-ol (9a). Method A. A suspension of $LiAlH_4$ (75 mg, 1.9 mmol) in dry THF (5 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled suspension was added dropwise with stirring a solution of **8a** (120 mg, 0.38 mmol) in dry THF (2 mL) during 10 min. After all of the reagents had been added, the resulting suspension was stirred at 0 °C for 15 min, at which time the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture then was stirred at ambient temperature for 7 h. The reaction mixture was quenched via careful, sequential addition of EtOAc (2 mL) and saturated aqueous NH_4Cl (5 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. Compound **9a** (75 mg, 92%) was thereby obtained as a colorless microcrystalline solid: mp 290−291 °C (dec) (sealed tube); IR (KBr) 3290 (m), 2939 (s), 2861 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J = 3.3 Hz, 2 H), 1.54 [t(*AB*), J_{AB} = 12.1 Hz, J = 3.7 Hz, 1 H], 1.58 (s, 1 H), 1.59 (t, J = 1.4 Hz, 2 H), 1.90 (A*B*, J_{AB} = 12.1 Hz, 1 H), 2.10 (t, J = 4.3 Hz, 1 H), 2.20−2.80 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 30.3 (t), 33.8 (t), 34.0 (d), 38.9 (d), 42.2 (t), 48.1 (d), 49.1 (d), 49.2 (d), 51.2 (d), 53.8 (d), 55.1 (d), 55.2 (d), 58.8 (d), 59.4 (d), 80.4 (s). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.18; H, 8.18.

Compound **9a** was further characterized via conversion into the corresponding 3,5-dinitrobenzoate derivative (**10a**). Thus, a solution of 3,5-dinitrobenzoyl chloride (74 mg, 0.32 mmol) in dry pyridine (1 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise with stirring a solution of **9a** (38 mg, 0.18 mmol) in dry CH_2Cl_2 (2 mL) during 5 min. After addition of reagents had been completed, the mixture was allowed to warm gradually to ambient temperature while stirring overnight. The reaction mixture was poured into ice−water (30 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (50 mL). The organic layer was washed sequentially with ice-cold 10% aqueous HCl (2 × 15 mL) and brine (15 mL), dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by using a 5−15% EtOAc−hexane gradient elution scheme.

The first chromatography fraction contained **10a** (37 mg, 50%), which was isolated as a colorless microcrystalline solid. Recrystallization of this material from EtOAc−hexane afforded analytically pure **10a** as a colorless microcrystalline solid; mp 194−195 °C; IR (KBr) 2950 (s), 2867 (w), 1720 (s), 1540 (vs), 1347 cm^{-1} (vs); ^{1}H NMR ($CDCl_3$) δ 1.59 [t(*AB*), J_{AB} = 12.2 Hz, J = 3.3 Hz, 1 H], 1.68 (s, 2 H), 1.78−1.82 (m, 2 H), 2.13 (A*B*, J_{AB} = 12.2 Hz, 1 H), 2.27 (t, J = 4.4 Hz, 1 H), 2.36−2.78 (m, 7 H), 2.80−2.94 (m, 3 H), 9.09 (d, J = 2.1 Hz, 2 H), 9.17 (t, J = 2.1, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.3 (t), 33.9 (d), 34.1 (t), 38.6 (d), 42.15 (t), 48.2 (d), 49.1 (d), 49.5 (d), 51.2 (d), 53.8 (d), 54.8 (d), 55.1 (d), 55.9 (d), 56.7 (d), 93.6 (s), 121.9 (d), 129.3 (d), 135.5 (s), 148.6 (s), 161.5 (s). Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94. Found: C, 64.59; H, 4.89.

Continued elution of the chromatography column afforded a second fraction which contained recovered **9a** (18 mg, 47%). Compound **9a** was thereby recovered as a colorless microcrystalline solid: mp 290−291 °C. The IR, ^{1}H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **9a** (*vide supra*).

Compound **9a** was further characterized via conversion into the corresponding *p*-nitrobenzoate derivative (**10b**). Thus, into a 10 mL round-bottom flask that previously had been flushed with argon was added a solution of *p*-nitrobenzoyl chloride (45 mg, 0.24 mmol) in dry pyridine (0.5 mL), and the reaction mixture was cooled to 0 °C via application of an external ice−water bath. To this cold solution was added dropwise with stirring a solution of **9a** (35 mg, 0.16 mmol) in dry CH_2Cl_2 (1.5 mL). After the addition of **9a** had been completed, the external cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature while stirring overnight. The reaction mixture was poured into ice water (20 mL), and the resulting aqueous suspension was extraced with CH_2Cl_2 (40 mL). The organic layer was washed sequentially with ice-cold 10% aqueous HCl (2 × 10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 5% EtOAc−hexane. Compound **10b** (30 mg, 52%) was thereby obtained as a colorless microcrystalline solid. Recrys-

tallization of this material from Et_2O afforded analytically pure **10b** as a colorless microcrystalline solid; mp 212−213 °C; IR (KBr) 2936 (m), 2860 (w), 1713 (vs), 1526 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.57 [t(*A*B), J = 12.1, 3.3 Hz, 1 H), 1.66 (s, 2 H), 1.77 (d, J = 3.22 Hz, 2 H), 2.11 (A*B*, J_{AB} = 12.1 Hz, 1 H), 2.20−2.30 (m, 1 H), 2.38−2.78 (m, 7 H), 2.80−2.92 (m, 3 H), 8.13 (*A*B, J_{AB} = 8.7 Hz, 2 H), 8.24 (A*B*, J_{AB} = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.4 (t), 33.9 (d), 34.1 (t), 38.8 (d), 42.2 (t), 48.2 (d), 49.2 (d), 49.6 (d), 51.2 (d), 53.8 (d), 54.8 (d), 55.2 (d), 55.9 (d), 56.7 (d), 92.0 (s), 123.4 (d), 130.5 (d), 137.2 (s), 150.3 (s), 163.8 (s). Anal. Calcd for $C_{22}H_{21}NO_4$: C, 72.71; H, 5.82. Found: C, 72.90; H, 5.92.

Continued elution of the chromatography column afforded a second fraction. Workup of this chromatography fraction gave pure **9a** (15 mg, 43%) as a colorless microcrystalline solid: mp 290−291 °C (dec, sealed tube). The IR, ^1H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **9a** (*vide supra*).

Compound **9a** was further characterized via conversion into the corresponding phenylurethane derivative (**10c**). Thus, a mixture of **9a** (43 mg, 0.20 mmol) and phenyl isocyanate (52 mg, 0.44 mmol) was heated at 60 °C with stirring during 2 h. The reaction mixture was allowed to cool to ambient temperature. Water (5 mL) was added to the reaction mixture, and the resulting mixture was stirred at ambient temperature for 2 h. The resulting aqueous suspension was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 5% EtOAc in hexane. Pure **10c** (63 mg, 94%) was thereby obtained as a colorless oil which slowly solidified upon standing at ambient temperature. Recrystallization of this material from hexane afforded analytically pure **10c** as a colorless microcrystalline solid; mp 80−81 °C; IR (KBr) 2943 (s), 2860 (w), 1699 (s), 1524 (s), 1443 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.47 [t(*A*B), J_{AB} = 12.2 Hz, J = 3.5 Hz, 1 H], 1.58 (s, 2 H), 1.62 (d, J = 3.4 Hz, 2 H), 1.99 (A*B*, J_{AB} = 12.2 Hz, 1 H), 2.14 (t, J = 4.5 Hz, 1 H), 2.24−2.68 (m, 7 H), 2.72−2.82 (m, 3 H), 6.47 (br s, 1 H), 6.90−7.00 (m, 1 H), 7.16−7.32 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 26.8 (t), 33.9 (d), 34.0 (t), 38.8 (d), 42.15 (t), 48.2 (d), 49.2 (d), 49.5 (d), 51.2 (d), 53.7 (d), 54.8 (d), 55.1 (d), 55.9 (d), 56.8 (d), 90.0 (s), 118.6 (d), 123.0 (d), 128.9 (d), 138.2 (s), 152.7 (s). Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95. Found: C, 79.46; H, 6.73.

Method B. A solution of *p*-TsCl (804 mg, 4.22 mmol) in dry pyridine (5 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise a solution of **4** (603 mg, 2.8 mmol) in dry CH_2Cl_2 (10 mL) during 15 min, and the reaction mixture then was allowed to warm gradually to ambient temperature while stirring overnight. The reaction mixture was poured into ice−water (50 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was washed with ice-cold 5 M aqueous HCl (2 × 15 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (20 mL), and silica gel (60−200 mesh, 15 g) was added to this solution. The resulting mixture was stirred at ambient temperature for 0.5 h to promote adsorption of the substrate onto the surface of the silica gel. The resulting suspension was placed onto a silica gel column (50 g, column dimensions 50 cm × 2 cm) and then was allowed to stand on the column at ambient temperature overnight. Subsequently, the chromatography column was eluted by using CH_2Cl_2 until all of the unreacted TsCl had been eluted, at which point elution of the chromatography column was continued by using 20% EtOAc−hexane. Pure **9a** (539 mg, 89%) was thereby obtained as a colorless microcrystalline solid: mp 290−291 °C (dec) (sealed tube). The IR, ^1H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **9a** (*vide supra*).

Method C. To a solution of **7** (179 mg, 0.49 mmol) in CH_2Cl_2 (10 mL) was added silica gel (60−200 mesh, 10 g), and the resulting mixture was stirred at ambient temperature for 0.5 h to promote adsorption of the substrate onto the silica gel surface. The resulting suspension was placed onto a silica gel column (40 g, column dimensions 50 cm × 2 cm) and then was allowed to stand on the column at ambient temperature overnight. The chromatography column was eluted by using 22% EtOAc−hexane. Pure **9a** (83 mg, 81%) was thereby obtained as a colorless microcrystalline solid; mp 290−291 °C (dec) (sealed tube). The IR, ^1H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **9a** (*vide supra*).

3-Iodoheptacyclo[7.6.0.0^{2,7}.0^{3,14}.0^{5,12}.0^{6,10}.0^{11,15}]pentadecane (11).[9] A solution of Ph_3P (225 mg, 0.86 mmol) and **9a** (0.92 mg, 0.43 mmol) in CH_2Cl_2 (5 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added portionwise I_2 (218 mg, 0.86 mmol), during 15 min, and the resulting mixture was stirred at 0 °C for 3 h. The external ice−water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature with stirring during 18 h. At that time, TLC analysis of the reaction mixture revealed the presence of unreacted **9a**. To drive the reaction to completion, the reaction mixture was refluxed with stirring for 24 h. The reaction mixture then was poured into hexane (40 mL), and the resulting mixture was extracted with 20% aqueous $Na_2S_2O_3$ (2 × 15 mL). The combined organic layers were washed successively with water (10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Compound **11** (113 mg, 81%) was thereby obtained as a colorless viscous oil which slowly solidified upon standing at ambient temperature. Low-temperature recrystallization of this material from Et_2O−MeOH afforded pure **11** as a colorless microcrystalline solid: mp 64−65 °C; IR (KBr) 3290 (m), 2939 (s), 2861 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.42 [t(*A*B), J_{AB} = 12.5 Hz, J = 3.8 Hz, 1 H], 1.61 (s, 2 H), 2.01−2.20 (m, 4 H), 2.25 (t, J = 4.5 Hz, 1 H), 2.32−2.44 (m, 1 H), 2.50−2.76 (m, 6 H), 3.30−3.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.7 (t), 37.4 (t), 38.0 (d), 38.8 (d), 42.1 (t), 47.6 (d), 48.1 (d), 49.8 (d), 51.2 (s), 51.5 (d), 53.8 (d), 55.0 (d), 55.1 (d), 65.7 (d), 65.9 (d). Anal. Calcd for $C_{15}H_{17}I$: C, 55.57; H, 5.29. Found: C, 55.53; H, 5.42.

Heptacyclo[7.6.0.0^{2,7}.0^{3,14}.0^{5,12}.0^{6,10}.0^{11,15}]pentadecane (12). To a solution of **11** (61 mg, 0.19 mmol) in dry toluene (5 mL) under argon were added sequentially (n-Bu)$_3$SnH (0.05 mL, 0.19 mol) and azobis(isobutyronitrile) (AIBN, 5 mg, catalytic amount). The resulting solution was refluxed for 10 min and then was allowed to cool gradually to ambient temperature with stirring during 1 h. The reaction mixture then was quenched by addition of saturated aqueous $NaHCO_3$ (2 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Pure **12** (30 mg, 80%) was thereby obtained as a colorless microcrystalline solid: mp 252−253 °C (sealed tube); IR (KBr) 2936 (vs), 2860 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.06 [t(*A*B), J_{AB} = 12.7 Hz, J = 2.4 Hz, 1 H], 1.21 [t(A*B*), J_{AB} = 12.7 Hz, J = 3.8 Hz, 1 H], 1.34 [t(*A*B), J_{AB} = 12.1 Hz, J = 3.7 Hz, 1 H], 1.60 (t, J = 1.5 Hz, 2 H), 1.76 (A*B*, J_{AB} = 12.1 Hz, 1 H), 1.78−1.84 (m, 1 H), 2.09−2.24 (m, 2 H), 2.32−2.68 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 21.1 (t), 33.4 (t), 34.4 (d), 36.9 (d), 42.9 (t), 49.2 (d), 50.3 (d), 51.6 (d), 54.3 (d), 55.2 (d). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.87; H, 8.91.

7-(*p*-Tosyloxymethyl)heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (13). A solution of *p*-TsCl (201 mg, 1.06 mmol) in dry pyridine (2 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise a solution of **5** (151 mg, 0.70 mmol) in dry CH_2Cl_2 (5 mL) during 15 min, and the reaction mixture then was allowed to warm gradually to ambient temperature while stirring overnight. The reaction mixture was poured into ice−water (30 mL), and the resulting aqueous suspension was extracted with CH_2Cl_2 (60 mL). The organic

layer was washed with ice-cold 5 M aqueous HCl (2 × 10 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with 30% CH_2Cl_2−hexane. Compound **13** (242 mg, 94%) was thereby obtained as a colorless microcrystalline solid. Recrystallization of this material from EtOAc−hexane afforded analytically pure **13** as a colorless microcrystalline solid: mp 115−116 °C; IR (film) 2960 (s), 2876 (m), 1614 (w), 1365 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.77 (s, 2 H), 2.28−2.48 (m, 15 H), 2.55 (t, J = 7.8 Hz, 1 H), 3.92 (d, J = 7.8 Hz, 2 H), 7.31 (*A*B, J_{AB} = 8.1 Hz, 2 H), 7.76 (A*B*, J_{AB} = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 43.0 (t), 50.3 (d), 50.6 (d), 51.1 (d), 52.0 (d), 52.2 (d), 53.0 (d), 53.1 (d), 55.0 (d), 71.8 (t), 127.8 (d), 129.7 (d), 133.3 (s), 144.5 (s). Anal. Calcd for $C_{22}H_{24}O_3S$: C, 71.71; H, 6.56. Found: C, 71.75; H, 6.62.

7-(Iodomethyl)heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (14).[9] **Method A.** To a solution of NaI (89 mg, 0.15 mmol) in dry ethylene glycol dimethyl ether (1 mL) under argon was added **13** (55 mg, 0.15 mmol). The reaction mixture was stirred at 65 °C for 4 h and was then allowed to cool gradually to ambient temperature while stirring overnight. Water (5 mL) was added, and the resulting aqueous suspension was extracted with CH_2Cl_2 (2 × 5 mL). The organic layer was washed with brine (5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Compound **14** (47 mg, 97%) was thereby obtained as a colorless microcrystalline solid. Low-temperature recrystallization of this material from Et_2O−MeOH afforded analytically pure **14** as a colorless microcrystalline solid; mp 64−65 °C; IR (KBr) 2945 (vs), 2866 (m), 1429 (w), 1290 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.80 (s, 2 H), 2.33−2.60 (m, 12 H), 2.71 (t, J = 8.2 Hz, 1 H), 3.15 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.8 (t), 43.1 (t), 49.9 (d), 50.3 (d), 51.2 (d), 52.7 (d), 52.8 (d), 53.6 (d), 55.4 (d), 59.4 (d). Anal. Calcd for $C_{15}H_{17}I$: C, 55.57; H, 5.29. Found: C, 55.76; H, 5.46.

Method B. A solution of Ph_3P (141 mg, 0.54 mmol) and **5** (0.58 mg, 0.27 mmol) in CH_2Cl_2 (1 mL) under argon was cooled to 0 °C via application of an external ice−water bath. To this cooled solution was added dropwise a solution of I_2 (137 mg, 0.54 mmol) in CH_2Cl_2 (5 mL), and the resulting mixture was stirred at 0 °C for 3 h. The external ice−water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature and then was refluxed for an additional 4 h. The reaction mixture then was poured into hexane (40 mL) and was extracted with 20% aqueous $Na_2S_2O_3$ (2 × 20 mL). The combined organic layers were washed successively with water (20 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Compound **14** (75 mg, 86%) was thereby obtained as a colorless oil which slowly solidified upon standing at ambient temperature. Recrystallization of this material from Et_2O−MeOH in freezer afforded pure **14** as a colorless microcrystalline solid: mp 64−65 °C. The IR, ^1H, and ^{13}C NMR spectra of this material are identical in all respects with the corresponding spectra obtained previously for authentic **14** (*vide supra*).

7-(Methylene)heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]-tetradecane (15). To a solution of Na (21 mg, 0.92 mmol) in absolute EtOH (5 mL) under argon was added **14** (75 mg, 0.23 mmol), and the resulting mixture was heated at 85 °C for 35 h. The reaction mixture was allowed to cool gradually to ambient temperature and was then concentrated *in vacuo*. Water (10 mL) was added to the residue, and resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by eluting with hexane. Pure **15** (14 mg, 79%) was thereby obtained as a colorless microcrystalline solid: mp 76−77 °C (lit.[3c] mp 78−79 °C). The IR, ^1H, and ^{13}C NMR spectra of this material are identical in all respects with the corresponding spectra reported previously for authentic **15**.[3c]

Acid-Promoted Rearrangement of 13. To a stirred solution of **13** (202 mg, 0.55 mmol) in $CHCl_3$ (15 mL) at ambient temperature was added CF_3CO_2H (3 mL, excess), and the resulting mixture was refluxed for 3 days. The reaction mixture was allowed to cool gradually to ambient temperature and then was quenched via careful addition of saturated aqueous $NaHCO_3$ (15 mL). Water (15 mL) was added, the layers were separated, and the water layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified via column chromatography on silica gel by using a 0−10% EtOAc−hexane gradient elution scheme.

Workup of the first chromatography fraction afforded pure 7-trifluoroacetoxyheptacyclo[7.6.0.0.^{2,6}0.^{3,14}0.^{4,12}0.^{5,10}0^{11,15}]-tetradecane (**18a**, 52 mg, 30%) as a colorless viscous oil; IR (film) 2951 (s), 2866 (m), 1776 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 1.50 [t(*A*B), J_{AB} = 15.0 Hz, J = 3.1 Hz, 1 H), 1.78 (t, J = 1.5 Hz, 2 H), 1.85−1.92 (m, 1 H), 1.98−2.32 (m, 8 H), 2.40−2.52 (m, 4 H), 5.21 (dt, J =10.1, 3.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.7 (t), 37.8 (d), 40.1 (d), 41.8 (t), 41.9 (d), 42.9 (d), 43.8 (d), 44.5 (d), 44.8 (d), 45.4 (d), 52.9 (d), 53.3 (d), 53.3 (d), 53.4 (d), 75.3 (s), 114.6 (q, $^1J_{CF}$ = 284.4 Hz), 157.3 (q, $^2J_{CF}$ = 41.6 Hz). Anal. Calcd for $C_{17}H_{17}F_3O_2$: C, 65.80; H, 5.52. Found: C, 65.89; H, 5.58.

Continued elution of the chromatography column afforded a second fraction. Workup of the second chromatography fraction afforded recovered (unreacted) **13** (130 mg, 64%) as a colorless microcrystalline solid: mp 115−116 °C. The IR, ^1H, and ^{13}C NMR spectra of the material thereby obtained were essentially identical to the corresponding spectra of authentic **13** (*vide supra*).

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Supporting Information Available: IR spectral data for a 3:1 mixture of **2** and **3** and for pure **4**−**7**, **8a**, **9a**, **10a**−**c**, **11**−**14**, and **18a**; 2-D ^1H−^1H COSY NMR spectrum of **18a** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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