Bromination of Decalin and Its Derivatives. 9. High Temperature Bromination

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Thermal and photobromination of decalin, **1**, was studied, *trans*,*cis*,*trans*-2,5,7,9-tetrabromooctalin, **2**, was obtained as the major product along with smaller amounts of bromonaphthalene derivatives. The structures of the products were determined by ^{1}H- and ^{13}C-NMR data and single X-ray structural analysis. Bromination of the two decalin derivatives **9** and **10** results in the formation of single isomers **11** and **12**, respectively. The three tetrabromides **2**, **11**, and **12** were shown by molecular mechanics calculations to be the most stable stereoisomer in each case. The formation of these tetrabromides under thermodynamic control is postulated.

Brominations of hydrocarbons are important processes because they lead to a variety of useful synthetic intermediates.[1] In the present investigation, we report conditions under which the bromination[2] of decalin, **1**, and several decalin derivatives proceeds with remarkable regio- and stereospecifity.

Decalin **1** is a saturated bicyclic hydrocarbon which occurs in diastereomeric cis and trans forms. Zelinsky and Turowa-Pollak[3] discovered that $AlBr_3$-catalyzed bromination of *cis*- and *trans*-decalin produced 1,2,3,5,6,7- and 1,2,3,4,6,7-hexabromonaphthalene, respectively. The correct structures of these molecules were determined by McKinney[4] and Ferguson.[5] In 1948, Barnes[6] reported the reaction of decalin with *N*-bromosuccinimide and isolated a tetrabromide whose structure was not reported. Stetter and Tresper[7] probably obtained the same product by the bromination of decalin in liquid bromine in the presence of catalytic amounts of hydrobromic acid. The correct structure of this compound remained unknown.

Results and Discussion

Decalin (from Merck Company, 62% cis, 38% trans isomer mixture) was heated to 150 °C and 5.0 equiv of bromine added over a 1.5 h period. The solution was stirred at the reaction temperature for an additional 30 min. The major product was tetrabromide **2** which was isolated by crystallization of the reaction mixture from hexane in a yield of 32%. After removing the unreacted starting material, the residue was subjected to repeated column chromatography, and four naphthalene derivatives were also isolated: 1,4-dibromnaphthalene (**3**),[8] 1,5-dibromnaphthalene (**4**),[8] 1,4,6-tribromonaphthalene (**5**),[9] and 1,4,5-tribromnaphthalene (**6**)[9] (Scheme 1). Although the starting material consisted of 62% *cis*-decalin, recovered unreacted decalin consisted mainly of *trans*-decalin, indicating that *cis*-decalin is more reactive than *trans*-decalin in the bromination reaction.

We also investigated the light-promoted radical reaction of bromine with decalin at temperatures of 50 and 10 °C using a sun lamp. Decreasing the reaction temperature increased the yield of tetrabromide **2** from 32% to 68%. The di- and tetrasubstituted naphthalene derivatives were also formed under these conditions but in lower yields.

Proton and carbon NMR studies of **2** indicated the formation of a highly symmetrical compound. The ^{1}H-NMR spectrum of **2** shows two sets of signals. The protons adjacent to bromine atoms appear as a doublet at 5.16 ppm (J = 2.7 Hz) and the methylene protons appear as a multiplet at 2.10−2.60 ppm. A three-line ^{13}C-NMR spectrum is also in agreement with the proposed structure and indicates the high symmetry in the molecule. However, on the basis of NMR data alone we were not able to distinguish between four possible symmetrical tetrabromides. Attempts to carry out reactions (epoxidation, bromination) with the central double bond in order to determine the structure of **2** resulted only in unreacted starting material. Apparently steric effects associated with the adjacent bromine atoms preclude reaction with the central double bond. However, the structure of tetrabromide **2** was finally determined by X-ray analysis[16] and is shown in Figure 2.

Since tetrabromide **2** is formally a result of sequential allylic brominations of octalin **8**, we propose that the reaction proceeds via the free radical bromination of **1** followed by dehydrobromination to generate **8** (Scheme 2). Subsequent allylic bromination of **8** then generates **2**.

In order to test this argument, we have carried out the bromination of **8** under the reaction conditions used for **2**. This reaction also produced **2** as the only diastereo-

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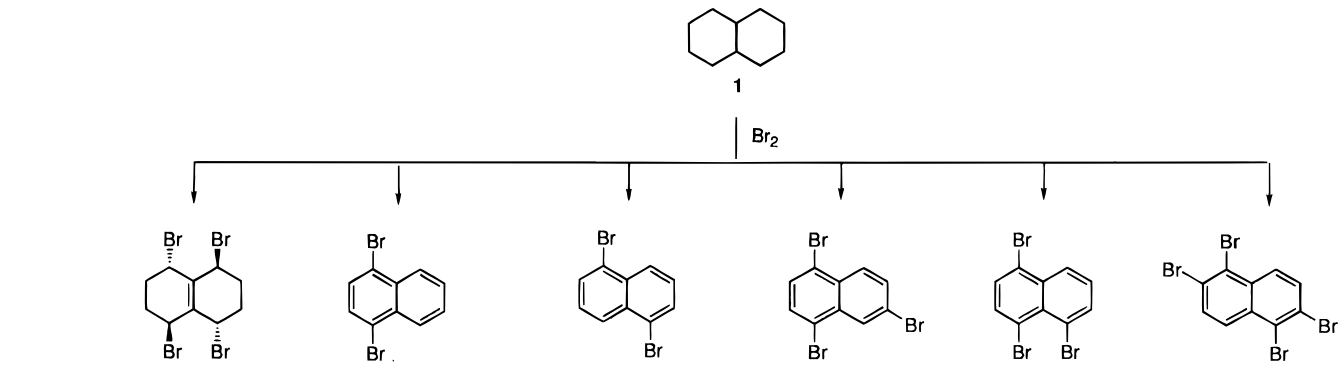
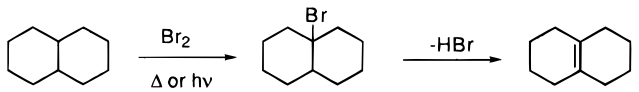
Scheme 1



	2	3	4	5	6	7
Br_2 / 150 °C	32%	14%	10%	5%	3%	—
Br_2 / hν/50 °C	48%	8%	5%	—	—	—
Br_2 / hν /10 °C	68%	3%	4%	—	—	2%

Scheme 2



meric allylic tetrabromide strongly supporting the intermediacy of **8** in the bromination of **1**.

That an allylic tetrabromide would accumulate as the bromination of **1** (and **8**) reaction proceeds is reasonable, as all of the allylic positions have been monobrominated, gem dibromide formation would be sterically unfavorable, and elimination of HBr (leading ultimately to bromonaphthalenes) may also be slow due to steric constraints. The exclusive formation of **2**, which is only one of the five possible diastereomeric tetrabromides could be a result of the fact that **2** is formed faster than the other diastereomers (kinetic control). Alternatively, **2** may simply be the most stable of the five possible diastereomeric allylic tetrabromides with sufficient time for an initially formed mixture of allylic tetrabromides to equilibrate (thermodynamic control).

In order to evaluate the relative stabilities of the diastereomeric 2,5,7,9-tetrabromobicyclo[4.4.0]dec-1,6-enes we have carried out molecular mechanics calculations with MMX force field.[10] Our computational investigation of these substituted octalins started with octalin itself. A previous MM2 study[11] of **8** showed that this molecule exists in the two conformers C_s and C_2 in Figure 1 with the C_s more stable by 0.3 kcal/mol. In the present investigation using the MMX force field, we also find the conformers to be close in energy, but the C_2 conformer was calculated to be the more stable by 0.3 kcal/mol.

Since the allylic hydrogens in **8** are in half-chair cyclohexenes, they are either pseudoaxial or pseudoequatorial (labeled A and E in Figure 1). Thus, there are two conformers of **2** derived from **8**-C_2 (all bromines axial and all bromines equatorial) and two enantiomeric conformers of **2** derived from **8**-C_s (two bromines axial and two bromines equatorial). In Figure 2, we have shown the MMX geometries of the three conformers whose energy would be expected to differ.

An examination of the structures in Figure 2 reveals that the conformer derived from **8**-C_2 with the bromines all in the pseudoaxial position is the most stable. It is not surprising that this conformation is the most stable one as dipole−dipole interactions often force bromines to be as far apart as possible. For example, 1,2-dibromocyclohexane is more stable in the diaxial than in the diequatorial conformation.[12] Furthermore, gauche-interactions of an axial cyclohexane substituent with an axial hydrogen atom become more stabilizing with an electronegative substituent. An electron rich bromine can attract an electron deficient axial hydrogen so that steric attraction among the axial substituents replaces steric repulsion. The calculations also indicate that energies of the three conformers vary inversely with the 1,3 dibromo distance, indicating that nonbonded interactions dominate the energy difference between the conformers (Figure 2).

If the energies of the other diastereomeric 2,5,7,9-tetrabromobicyclo[4.4.0]dec-1,6-enes derived from **8** also vary inversely with the 1,3 Br−Br distances, we may expect that the diastereomer corresponding to **2**, with all of its bromines trans, would have the greatest 1,3 Br−Br distance and hence be the most stable of the stereoisomers. The results of MMX calculations, shown in Figure 3, bear out this expectation. Diastereomer **2** has the greatest 1,3 Br−Br distance and is calculated to be the most stable.

In order to further clarify the remarkable stereospecificity observed in these tetrabrominations, we treated *syn*- and *anti*-octalin derivatives **9** and **10** with bromine at high temperature (77 °C) and in both cases isolated only one diastereomeric tetrabromide. Bromination of **9**[14] gave exclusively **11** while **10** yielded only **12**[15] (Scheme 3).

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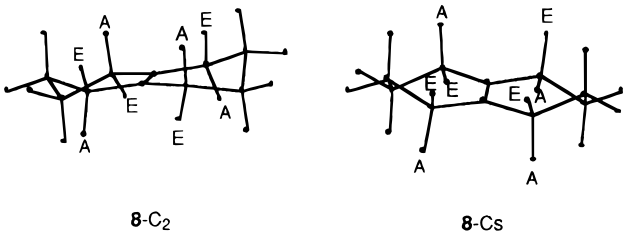
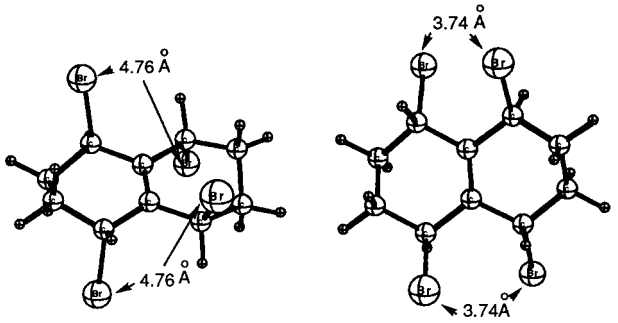
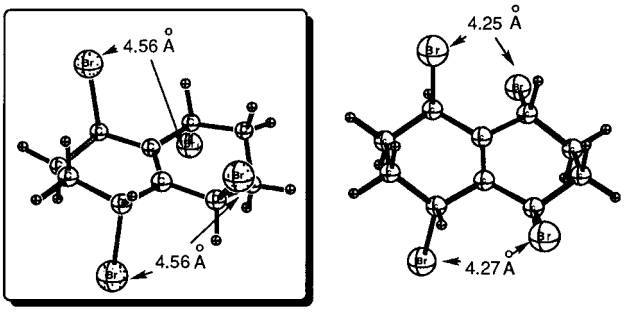


Figure 1. Two conformers of **8**.



2 derived from **8**-C_2 All Br axial
Rel E= 0.0 kcal/mol

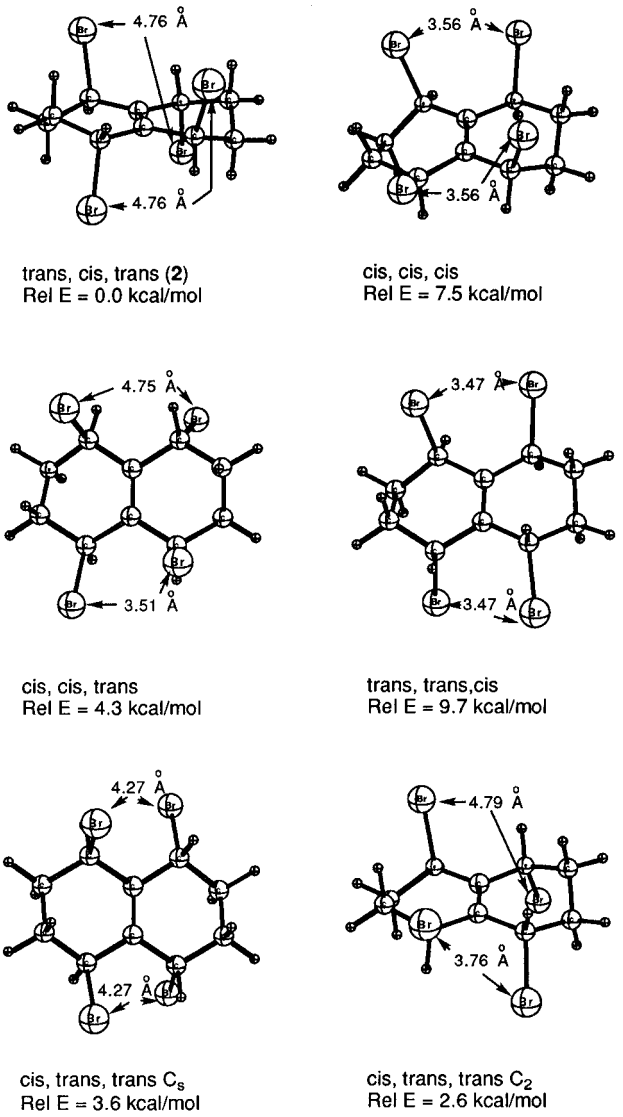
2 derived from **8**-C_2 All Br equatorial Rel E= 5.2 kcal/mol



X-Ray crystal structure of **2**

2 derived from **8**-C_s two Br equatorial and two Br axial
Rel E= 3.5 kcal/mol

Figure 2. Three possible conformers of **2** and their MMX relative energies and the X-ray crystal structure of **2**.



trans, cis, trans (**2**)
Rel E = 0.0 kcal/mol

cis, cis, cis
Rel E = 7.5 kcal/mol

cis, cis, trans
Rel E = 4.3 kcal/mol

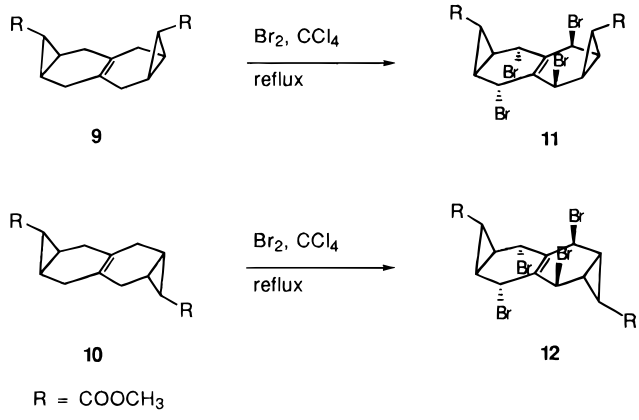
trans, trans,cis
Rel E = 9.7 kcal/mol

cis, trans, trans C_s
Rel E = 3.6 kcal/mol

cis, trans, trans C_2
Rel E = 2.6 kcal/mol

Figure 3. Geometries and relative MMX energies of the five diastereomeric 2,5,7,9-tetrabromobicyclo[4.4.0]deca-1,6-dienes.

Scheme 3



The assignment of the structures to **11** and **12** was accomplished by ^{1}H- and ^{13}C-NMR spectral data and NOE-measurements which were straightforward. The ^{1}H NMR spectrum of **11** showed two sets of signals for the methine, the cyclopropane, and the methyl protons. The 11-line ^{13}C NMR spectrum supports the proposed structure and symmetry in the molecule. The syn and anti relationship of the cyclopropyl hydrogens was confirmed by observation of NOE effects. Irradiation at the resonance signal of methine protons adjacent to bromine atoms at $\delta = 5.55$ caused signal enhancement at the resonances of the adjacent cyclopropane protons at $\delta = 2.59$ and the other cyclopropane proton at $\delta = 1.63$. However, irradiation at $\delta = 5.40$ caused signal enhancement only of the adjacent cyclopropane protons resonating at $\delta = 2.75$. These observations clearly indicate that two of the bromine atoms have a syn orientation with respect to the cyclopropane ring whereas the other two have an anti orientation. The fact that **12** has 6 ^{13}C NMR signals confirms the structure.

Figure 4 shows MMX-calculated geometries of these isomers in which both have the 2−10 and 5−7 bromines trans to one another. Table 1 shows the calculated MMX

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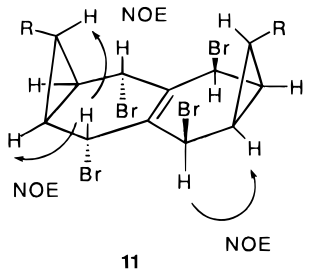
(16) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 1. The AM1 Calculated Heats of Formation and MMX Relative Steric Energies in kcal/mol of Diastereomeric Tetrabromides

AM1	MMX	AM1	MMX	AM1	MMX
5.9	7.5	80.23	8.21	82.65	4.95
2.64	9.7	76.09	9.75	77.87	8.04
1.03	0.0	74.96	6.74	75.08	3.65
0.91	2.6	74.91	11.53	73.98	5.74
0.65	4.3	73.26	5.76	73.40	2.07
		72.08	3.81	72.46	4.40
		69.26	0.00	72.04	0.00

energies of all possible diastereomers. In each case the diastereomer which is observed is the one calculated to be the most stable.

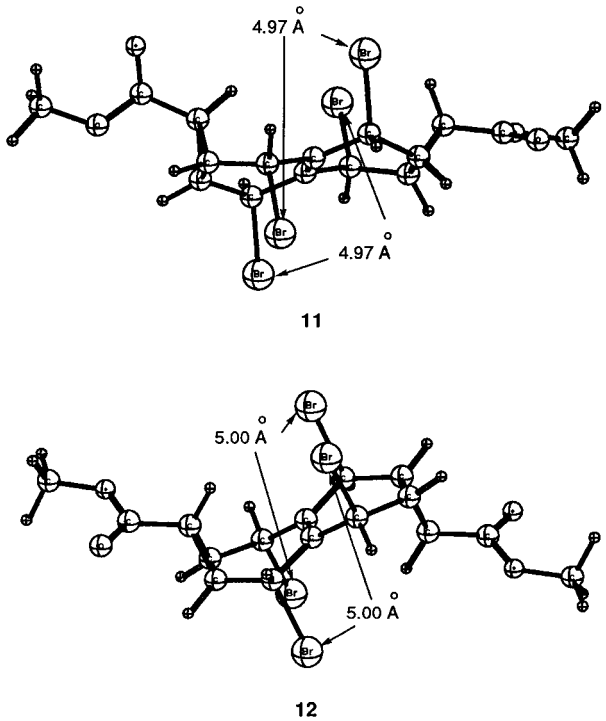


11

Although these calculations demonstrate that the most stable tetrabromide is formed exclusively in all cases, it may well be that these are also the kinetically controlled products. Once the first bromine is placed on an allylic position, it may direct the second bromine trans to it either three or four carbons removed. If this trans directing effect continues as subsequent bromines are placed on the ring, the diastereomer with all bromines trans would result. Such a kinetically controlled trans bromination causing the bromines to be as far as apart as possible could result from steric effects, bromine bridging in the radical, or a combination of these factors.

Conclusion

These experiments demonstrate that brominations carried out at high temperatures or photochemically, which are unencumbered by competing ionic reactions, can occur with remarkable stereo- and regiospecifity.



11 **12**

Figure 4. MMX calculated geometries of tetrabromides **11** and **12**.

Calculations and product analysis indicate that a major factor contributing to this specifity is the steric bulk of the bromines which dictates that products with these atoms as far apart as possible will predominate.

Experimental Section

Bromination of Decalin at 150 °C. To 20 g (0.14 mol) of decalin was added dropwise and over 1.5 h 116 g (0.72 mol) bromine at 150 °C while stirring. The resulting solution was stirred at the same temperature for an additional 30 min. After cooling to room temperature, the mixture was treated with 30 mL of hexane and allowed to stand one day in the refrigerator. Pure tetrabromide **2** (12 g, 24.5%) crystallized.

1a,4b,5a,8b-Tetrabromo-1,2,3,4,5,6,7,8-octahydronaphthalene (2): colorless crystals from chloroform/hexane (1:2), mp 185.5−186 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.16, (d, J = 2.7 Hz, H_1,H_4, H_5, and H_8), 2.10−2.60 (AA′BB′ system, 8H, H_2, H_3, H_6, and H_7); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.5, 49.5, 28; MS (70 eV) *m*/*z* 375/373/371/369 (M^+ − Br, 8) 293/291/289, (M^+ − 2Br, 8) 213/211, (M^+ − 3Br, 27) 131/129, (M^+ − 4Br, naphthalene, 100) 128; IR (KBr, cm^{-1}) 2995, 2905, 2835, 1423, 1335, 1200, 1170, 1000, 895, 743.

After removal of **2** by filtration, the residue was distilled to remove unreacted decalin (5 g). The residue was subjected to silica gel (130 g) chromatography, eluting with *n*-hexane. The first fraction consisted of 1,4-dibromonaphthalene (**3**), 1,5-dibromonaphthalene (**4**), and 1,4,6-tribromonaphthalene (**5**). After evaporation of the solvent, the residue was dissolved in methylene chloride/hexane and allowed to stand in a refrigerator causing **5** to crystallize.

1,4,6-Tribromonaphthalene (5): 1.98 g (5%), yellow crystals, mp 86−87 °C (lit. 86−87 °C[9]); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.36, (d, J_{57} = 1.9 Hz, 1H, H_5), 8.04 (d, J_{78} = 9.0 Hz, 1H, H_8), 7.65 (d, J_{78} = 9.0 Hz, 1H, H_7), 7.58 (m, 2H, H_2 and H_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 134.29, 132.02, 131.91, 131.53, 130.88, 130.36, 129.98, 123.47, 122.95, 121.67.

After removal of **5** by filtration, the residue was analyzed by ^{1}H-NMR spectroscopy which showed a mixture of 1,4-dibromonaphthalene (4.35 g, 14%) and 1,5-dibromonaphthalene (3.11 g, 10%). After repeated column chromatography (silica gel, hexane), both isomers were isolated as pure compounds.

1,4-Dibromonaphthalene (3): pale yellow crystals, mp 80−81 °C (lit. 81−82 °C[8]); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.26−7.61 (AA′BB′ system, 4H, H_5), 7.61 (s, 2H, H_2 and H_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.37, 130.57, 128.65, 128.25, 123.09.

1,5-Dibromonaphthalene (4): pale yellow crystals, mp 128−129 °C (lit. 131 °C[8]); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.21 (d, J = 8.1 Hz, 2H), 7.83 (d, J = 7.0, 2H), 7.41 (t, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.51, 131.38, 127.89, 127.79, 123.52.

The second fraction isolated was 1,4,5-tribromonaphthalene (**6**). **1,4,5-Tribromonaphthalene (6):** 1.2 g (3%), yellow crystals, mp 80−81 °C (lit. 85−86 °C[14]); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.36, (dd, J_{78} = 8.5 Hz, J_{68} = 1.2 Hz, 1H, H_8), 8.01 (dd, J_{67} = 7.5 Hz, 1H, H_6), 7.77 (d, J_{23} = 8.1 Hz, 1H,), 7.60 (d, 1H), 7.38 (dd, 1H, H_7); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.29, 137.24, 137.16, 137.02, 132.76, 130.94, 129.63, 125.61, 122.17, 121.53.

As the third fraction, 3.72 g of tetrabromide **2** was isolated (total yield 32%).

Photochemical Bromination of Decalin at 50 °C. To 20 g (0.14 mol) of decalin was added dropwise over 1 h 116 g (0.72 mol) of bromine at 50 °C while the reaction flask was irradiated with two 150 W sun lamps. The resulting solution was photolyzed at the same temperature for five days while the temperature was controlled by an internal thermometer. After cooling to room temperature, the mixture was treated with 30 mL of hexane and allowed to stand one in day in a refrigerator. Tetrabromide **2** (16 g, 43%) crystallized. After filtration of **2**, unreacted decalin (8.6 g) was removed by distillation and the residue subjected to silica gel (130 g) chromatography eluting with *n*-hexane. The first fraction was a mixture consisting of 1,4-dibromonaphthalene **3** (1.9 g, 8%) and 1,5-dibromonaphthalene **3** (1.2 g, 5%). The second fraction was identified as tetrabromide **2** (1.92 g, total yield 48%).

Photochemical Bromination of Decalin at 10 °C. To 4 g (0.029 mol) of decalin was added dropwise over 30 min 23.2 g (0.145 mol) bromine at 10 °C while the reaction flask was irradiated with two 150 W sun lamps. The resulting solution was photolyzed at the same temperature for seven days while the temperature was controlled by an internal thermometer. After cooling to room temperature, the formed precipitate of tetrabromide **2** was filtered (4.5 g). After filtration of **2**, unreacted decalin (1.5 g) was removed by distillation. The residue was treated with 10 mL of hexane and allowed to stand one day in a refrigerator. Additional tetrabromide **2** (1.07 g) crystallized (total 5.57 g, 68%) and the residue subjected to silica gel (120 g) chromatography eluting with *n*-hexane.

The first fraction was a mixture consisting of 1,4-dibromonaphthalene **3** (156 mg, 3%) and 1,5-dibromonaphthalene **3** (207 mg, 4%). This ratio was determined by ^{1}H-NMR spectroscopy. The second fraction was identified as tetrabromide **7**.

1,2,5,6-Tetrabromonaphthalene (7): 261 mg (2.5%), pale yellow crystals, mp 175−177 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17 (d, A-part of AB-system, J_{34} = J_{78} = 9.0 Hz, 2H), 7.74 (d, B-part of AB-system, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.40, 132.87, 129.50, 125.77, 125.46; IR (KBr, cm^{-1}) 3040, 3000, 2980, 1920, 1420, 1308, 1220, 1195, 1168, 1120, 1100, 895, 810. Anal. Calcd for $C_{10}H_4Br_4$: C, 28.07; H, 0.91. Found: C, 27.81; H, 0.86.

Bromination of *syn*-Dimethyl Tetracyclo[5.5.0.0^{3,5}.0^{9,11}]-dodec-1(7)ene-4,10-dicarboxylate at 77 °C. Compound **9** (1 g, 3.62 mmol) was dissolved in 25 mL of CCl_4 in a 50 mL two-necked flask equipped with reflux condenser and inlet glass tube touching the bottom of the reaction flask. The inlet glass-tube was connected to a 25 mL round-bottomed flask which contained 13 g (81.25 mmol) of bromine. Bromine vapor, obtained by heating of the flask to 100 °C, was transferred directly into CCl_4 solution at a temperature of 77 °C over 10 min while stirring magnetically. The reaction mixture was refluxed for 1 h. After cooling of the reaction mixture to 10 °C, tetrabromide **11** precipitated and was removed by filtration. The solvent was evaporated, and 50 mL of CH_2Cl_2 and 75 mL hexane were added. The CH_2Cl_2/hexane solution was allowed to stand for 15 h at 20 °C. Tetrabromide **11** that crystallized was removed by filtration. Colorless crystals from $CHCl_3$/ether: mp 186−187 °C; (1.41 g, 63%) ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.45 (m, 2H), 5.40 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.75 (m, 2H), 2.59 (m, 2H), 1.89 (t, J = 4.9 Hz, 1H), 1.63 (t, J = 4.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.33, 170.93, 131.23, 53.09, 52.89, 47.53, 43.57, 35.17, 32.26, 27.19, 24.89.

Bromination of *anti*-Dimethyl Tetracyclo[5.5.0.0^{3,5}.0^{9,11}]-dodec-1(7)ene-4,10-dicarboxylate at 77 °C. Compound **10** (5 g, 18.1 mmol) in 250 mL of CCl_4 was brominated using the procedure described above. The solvent was removed, and 50 mL CH_2Cl_2 and 75 mL hexane were added. The CH_2Cl_2/hexane solution was allowed to stand for 15 h at 20 °C. Tetrabromide **12** was removed by filtration. Colorless crystals (8.01 g, 75.0%) from $CHCl_3$/ether: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.94 (m, 4H), 3.70 (s, 6H), 2.58 (m, 4H), 1.72 (t, J = 4.05 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.99, 129.79, 52.87, 43.16, 27.89, 24.53.

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