Pergamon

Tetrahedron 55 (1999) 12853–12864

TETRAHEDRON

Bromination of Naphthalene and Derivatives: High Temperature Bromination XI*

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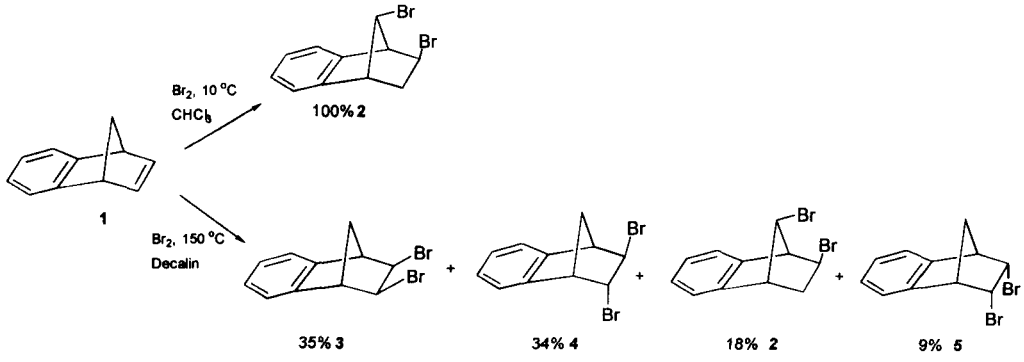
Received 8 June 1999; revised 6 August 1999; accepted 26 August 1999

Abstract: Thermal and photobromination of naphthalene and derivatives have been studied. Several hexabromo- (**12, 13, 16** and **17**), and tetrabromotetralin derivatives (**23, 24,** and **25**) have been obtained as the major products, besides bromonaphthalene derivatives. Base-promoted elimination reactions of **12, 13, 16** and **17** provided di- (**8**) tri- (**10**) and tetrabromo-naphthalenes (**22**). A convenient method was developed for the synthesis of 1,3-dibromonaphthalene (**26**) starting from (**24**). The structures of these products were determined by ^{1}H-,^{13}C- NMR data and X-ray structural analysis.

Keywords: Naphthalene, Bromination

Introduction

Bromination of hydrocarbons is an important process because it leads to useful intermediates for the synthesis of a large variety of bromoorganic compounds.[1,2] These materials have numerous industrial applications as pesticides, plastics, fire retardants, and pharmaceutical chemicals. In connection with our continuing interest in high temperature bromination reactions of unsaturated bicyclic systems we recently noticed that the reaction temperature has a dramatic influence on the product distribution.[3]



Scheme 1

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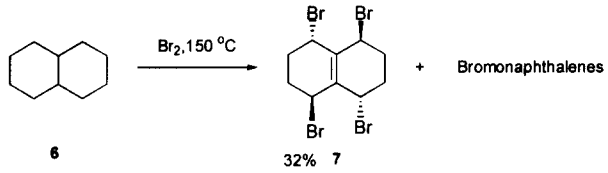
PII: S0040-4020(99)00758-9

For example, bromination of benzonorbornadiene (**1**) at room temperature or lower gave only rearranged product (**2**) in almost quantitative yield.[4] However, high temperature bromination of (**1**) at 150 °C resulted in the formation of non-rearranged products **3, 4, 5** and rearranged product **2** in a ratio of 4:1 (Scheme 1). Conducting the bromination reaction in the presence of free radical inhibitors suppressed the formation of the non-rearranged products.[4,5] This strongly supports the assumption that there is a competition between the radical and ionic mechanisms and that high temperature bromination is occurring by a free radical mechanism. Since radical intermediates are much less likely to rearrange, at higher temperatures we obtained mostly non-rearranged products. Furthermore, we studied high temperature bromination of decalin (**6**) and obtained 1,4,5,8-tetrabromooctalin **7** as the major product along with a smaller amount of bromonaphthalene derivatives.[6]



Scheme 2

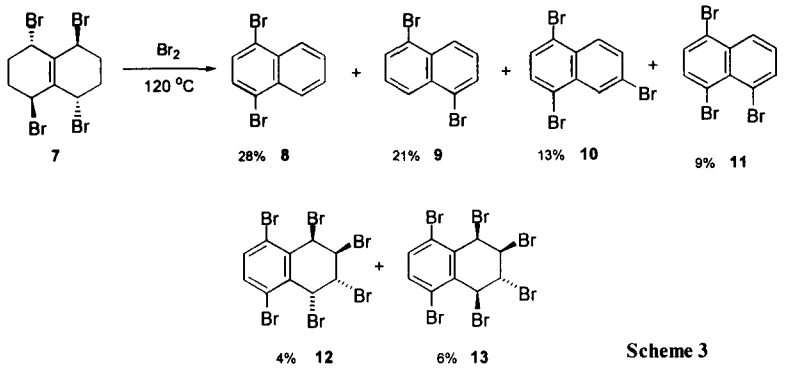
In view of the synthetic potential of highly substituted bromonaphthalenes and of high temperature bromination we have studied the bromination reaction of (**7**) and naphthalene at higher temperatures.

Bromination of naphthalene has been studied by several research groups.[7,8] Zalkind and Faerman[9] have examined the bromination of naphthalene under different reaction conditions and they isolated 1,4-dibromonapthalene (**8**) and 1,5-dibromonapthalene (**9**). Further bromination of 1,4-dibromonaphthalene gave hexabromonaphthalenes and octabromonaphthalene, the structures of which were not reported. Yanovskaya[10] has reported the quantitative preparation of 1,4-bromonaphthalene by the reaction of naphthalene with dioxane dibromide in 1:2 mole ratio, at 40 °C. However, in 1958, Bayer and O'Reilly[11] repeated the same reaction and reported contrary to the findings of Yanovskaya the formation of 1-bromonaphthalene[8], and 1,4-dibromonapthalene (**8**) and 1,5-dibromonapthalene (**9**). Zelinsky and Turowa-Pollak[12] discovered that $AlBr_3$-catalysed bromination of *cis*-, and *trans*-decalin produced 1,2,3,5,6,7- and 1,2,3,4,6,7-hexabromonaphthalene, respectively. 1,2,3,4,6,7-Hexabromonaphthalene was also obtained from the $AlBr_3$-catalysed bromination of naphthalene. The structures of these molecules were determined by McKinney[13] and Hamill and their co-workers.[14] McKinney *et al.*[13] obtained the same product (1,2,3,4,6,7-hexabromonaphthalene) by the iron powder catalysed bromination of naphthalene. Photobromination of naphthalene has been investigated by Sampey *et al.*[15] and Mayo and Hardy.[16] They obtained tetrabromonaphthalene. The correct structure of this compound remains unknown.

In this paper we report full details on the bromination of naphthalene at high temperature.

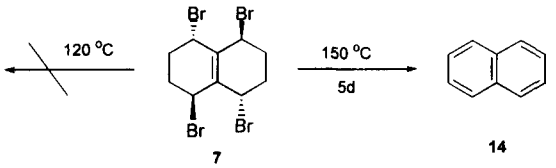
Results and Discussion

First, the bromination of the tetrabromide **7** was investigated. Tetrabromide **7** which was obtained from the bromination of decalin, was heated to 120 °C, and 1.2 equiv. of bromine was added over 1.5 h. The solution was stirred at the reaction temperature for an additional 30 min.



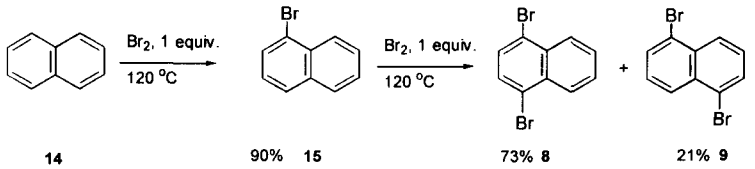
Scheme 3

The ^{1}H-NMR spectral analysis of the reaction mixture indicated the formation of six naphthalene derivatives: 1,4-dibromonaphthalene (**8**),[9] 1,5-dibromonaphthalene (**9**),[9] 1,4,6-tribromonaphthalene (**10**),[7] 1,4,5-tribromonaphthalene (**11**)[7] and the hexabromonaphthalene derivatives **12** and **13** (Scheme 3). These products may be formed either by direct bromination of tetrabromide **7**, followed by HBr elimination or **7** can be converted directly to naphthalene (**14**) which can undergo bromination to provide various naphthalene derivatives (**8, 9, 10, 11, 12**, and **13**). In order to test the stability of the starting material, tetrabromide **7** under the given reaction temperature, we heated **7** for many hours at 120 °C. We could not observe any dehydrobromination reaction. However, prolonged heating (5 days) of **7** at 150 °C gave smoothly naphthalene (Scheme 4). But, even this observation can not exclude the formation of naphthalene which can undergo further bromination reactions. It can be assumed that bromine can catalyze the dehydrobromination reaction of **7** to give naphthalene. Therefore, we decided to study bromination of naphthalene at 120 °C with various amounts of bromine.



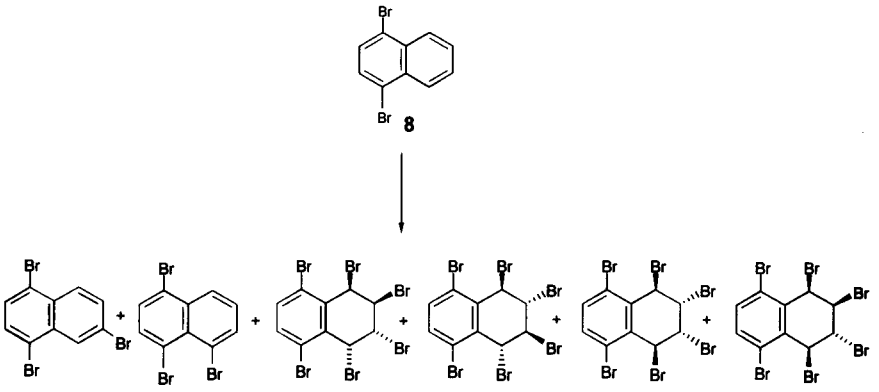
Scheme 4

Bromination of naphthalene at 120 °C with 1 equiv. bromine gave 1-bromonaphthaline (**15**) in 90 % yield as the sole product (Scheme 5). Further bromination of this formed monobromide **15** at 120 °C with 1 equiv. bromine afforded two dibromonaphthalene isomers which were characterized as 1,4- and 1,5-dibromonaphthalenes (**8**) and (**9**) in 73 and 21% yields, which were easily separated by crystallization.



Scheme 5

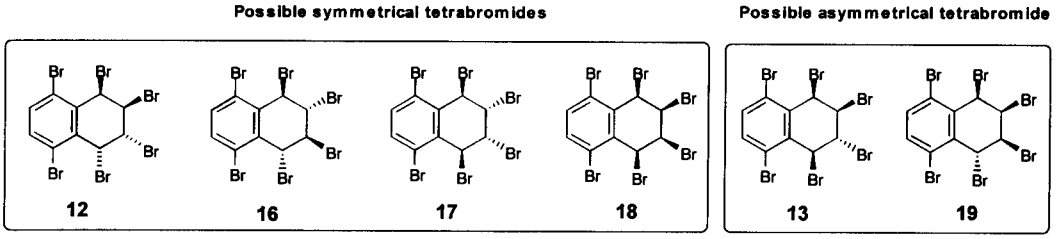
The major component **8** of this reaction was submitted separately to further bromination reaction at 120 °C without solvent. The ^{1}H-NMR studies of the reaction mixture revealed that five products **10, 11, 12, 13 and 17** were formed. Carefully repeated fractional crystallization combined with column chromatography allowed us to isolate all the formed products: three saturated hexabromides **12, 13,** and **17** and two tribromides **10** and **11** (Scheme 6). Decreasing the reaction temperature increased the yields of saturated hexabromides.



	10	**11**	**12**	**16**	**17**	**13**
Br_2/ 120 °C	21%	13%	20%	-	3%	13%
Br_2/ hv/CCl_4/r.t.	-	-	5%	-	93%	1%
Br_2/ hv/r.t.	-	-	14%	8%	14%	54%

Scheme 6

Furthermore, we studied the photochemical bromination of dibromide **8** under different reaction conditions (with solvent and without solvent) using a sun lamp (150 Watt) and obtained only saturated hexabromides **12, 13, 16,** and **17** in nearly quantitative yield. ^{1}H- and ^{13}C-NMR spectral studies on **12, 16** and **17** indicate their high symmetry. The ^{1}H-NMR spectra of these compounds show two sets of signals (Figure 1). The aromatic protons appear as singlets and the aliphatic protons give rise to AA'BB' systems in all three cases indicating the high symmetry in these molecula. Five line ^{13}C-NMR spectra are also in agreement with the proposed structures. On the basis of these spectral data, we were not able to distinguish between the four possible symmetrical structures **12, 16, 17,** and **18**.



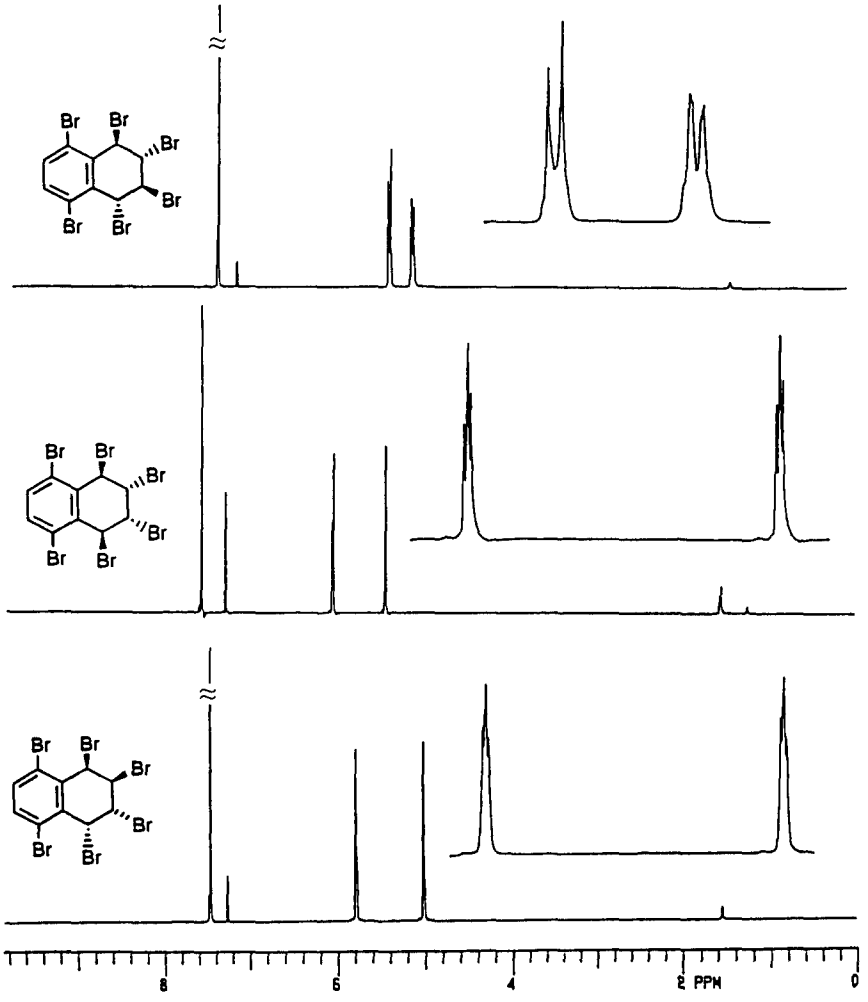
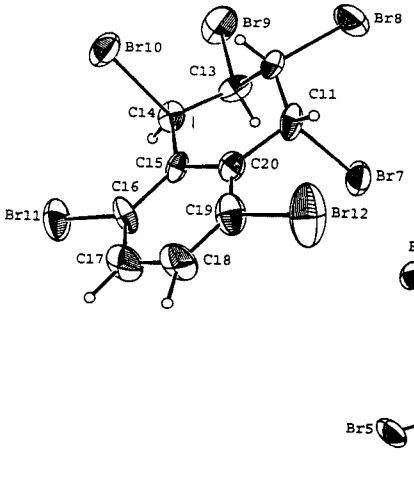


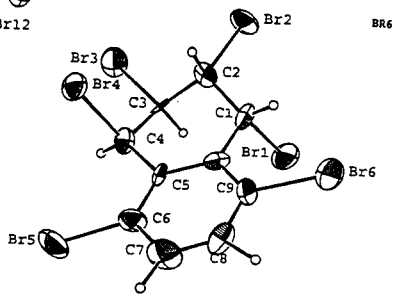
Figure 1. 200 MHz ^{1}H-NMR spectra of **16**, **17**, and **12**.

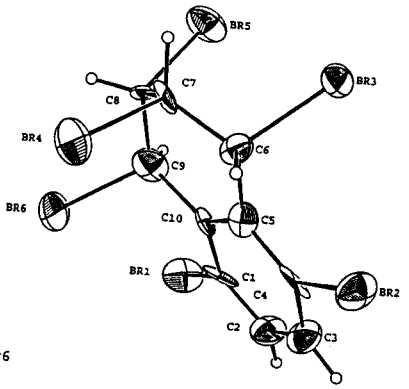
Therefore, the structural assignment to hexabromides **12** and **16** was established by X-ray crystallographic analyses (Figure 2 and 3). The hexabromide **12** can adopt two different conformation either aeea or eaae. The crystallographic analysis indicates that the bromine atoms in **12** have the aeea conformation as suggested by Abraham for the conformation of conduritol-D.[17] For the third symmetrical compound, two possible structures can be considered, which are **17** and **18**. The structure **18** can be ruled out on the basis of steric factors. In order to support this conclusion we have carried out AM1 calculations[18] on both hexabromides **17** and **18**. Results from AM1 calculations show that the isomer **17** is 12.9 kJ/mol more stable than the isomer **18** (Figure 3).

For the asymmetrical hexabromide, there are two possible isomeric structures **13** and **19**. The complete analysis of the first order ^{1}H-NMR spectrum indicated a large coupling constant (J_{23} = 11.3 Hz) for the protons bonded to C_2- and



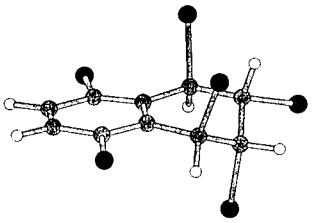
(12)



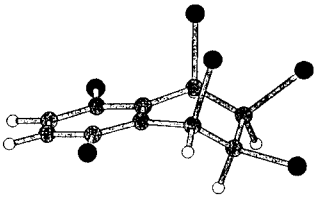


(16)

Figure 2. X-ray crytal structures of **12** and **16**



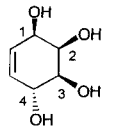
(**17**): AM1 Geometry optimizatization
Rel. E = 0.0 kJ/mol



(**18**): AM1 Geometry optimization
Rel. E = 12.9 kJ/mol

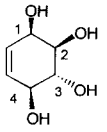
Figure 3. Geometries and relative energies of two diastereomeric tetraline hexabromides **17** and **18.**

C_3-atoms which strongly supports axial-axial alignment of the protons. In other words, bromine atoms prefer equatorial positions. Abraham *et al.*[17] have performed complete ^{1}H-NMR analysis of the all possible conduritol derivatives and found that a similar coupling (J_{23} = 11.0 Hz) for conduritol-F.[19] In the case of cis-configuration (conduritol-C[20]) of hydroxyl groups (axial-equatorial), the measured coupling constant was 2.1 Hz. This comparison indicates clearly that the isolated asymmetrical hexabromide **13** has the *cis,trans,trans*-configuration.



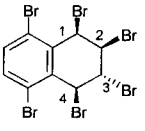
J_{23} = 2.1 Hz

20 Conduritol-C



J_{23} = 11.0 Hz

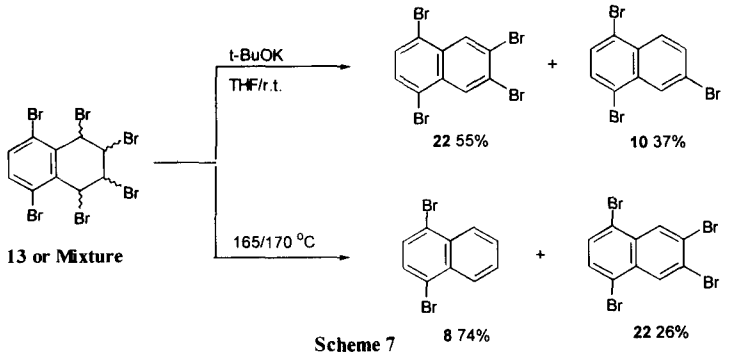
21 Conduritol-F



J_{23} = 11.3 Hz

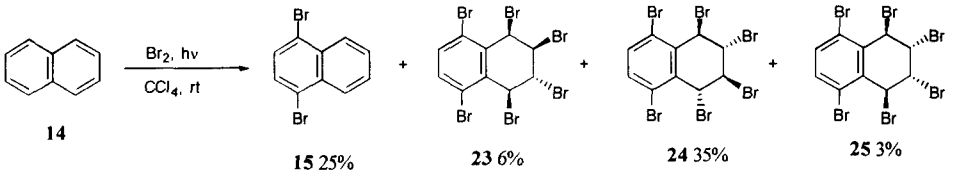
13

After successful isolation and characterization of these hexabromides which have the requisite skeletal arrangement and functionality to permit the easy introduction of two double bonds to form naphthalene derivatives, we submitted either pure isomers or an isomeric mixture consisting of **12, 13, 16,** and **17** to a dehydrobromination reaction with 2 mol of potassium *tert*-butoxide and isolated **22** and **10** in 55 and 37% yields which were easily separated by crystallization. Structural assignment to **22** was achieved my means of ^{1}H- and ^{13}C-NMR data.



Scheme 7

However, direct heating (165-170 °C) of a mixture **12, 13,** and **17** resulted in the formation of a mixture consisting of **8** and **10** *via* HBr or Br_2 elimination (Scheme 7).



Scheme 8

Finally, naphthalene (**14**) was submitted to photobromination. To a stirring solution of naphthalene (**14**) in carbon tetrachloride was added a solution of bromine in carbon tetrachloride while irradiating with a 150 W sun lamp. Carefully repeated fractional crystallization combined with column chromatography allowed us to isolate all the formed products. According to ^{1}H-NMR spectral data and elemental analysis, three isomeric tetrabromides **23, 24,** and **25** were formed beside 1-bromonaphthalene (**15**) (Scheme 8). The structure of the asymmetrical tetrabromide **23** was established easily by measuring of the vicinal coupling constant J_{23} = 11.3 Hz which indicates the *trans* configuration of the bromine atoms at C-2 and C-3 carbon atoms which is only in agreement with the proposed asymmetrical structure **23**. The structure of the major isomer **24** was determined by the X-ray crystallographic analyses (Figure 4). The structure of the minor product **25** formed with 3% yield was established by comparison of its ^{1}H-NMR spectrum with those of **17**. Furthermore, AM1 calculations on the tetrabromide **25** and the other possible all *cis*-isomer indicated the first one 9.6 kJ/mol is more stable than the other isomer.

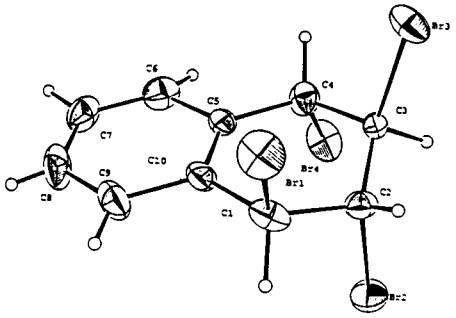
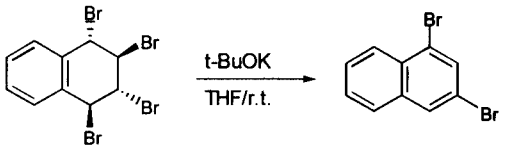


Figure 4. X-ray crytal structures of **24**



24 **Scheme 9** **26** 87%

Tetrabromide **24** was treated with potassium-*tert*-butoxide in THF and 1.3-dibromonaphthalene **26** obtained in high yield.

Conclusion

These experiments demonstrate that bromination of naphthalene with one mol bromine at 120 °C can occur with remarkable regiospecifity to afford 1-bromonaphthalene (**15**). However, bromination with 2 mol bromine at the same temperature afford a mixture of 1,4-bromo- (**8**) and 1,5-bromonaphthalene (**9**) in a ratio of (4:1) which can be separated easily by crystallization. Bromination of 1,4-dibromonaphthalene (**8**) with excess bromine at 120 °C provides three isomeric tetrabromides beside the tribromides. Base induced elimination of these tetrabromides formed 1,4,6-tribromonaphthalene (**10**) and 1,4,6,7-tetrabromonaphthalene (**22**). This methodology can be applied to the synthesis of tetrabromide **22**. Direct photobromination of naphthalene gave three tetrabromides where the symmetrical one **24** appears as the major product. Base induced elimination of **24** gave 1,3-bromonaphthalene (**26**) which is a short way for the synthesis of (**26**).

Experimental

Melting points were determined on a Thomas-Hoover capillary melting apparatus and are uncorrected. Infrared spectra were obtained from solution in 0.1mm cells or KBr pellets for solids on a Perkin-Elmer 337 infrared recording spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were recorded on 200 (50)-MHz Varian spectrometer and reported in δ units with $Si(CH_3)_4$ as internal standard. All column chromatography was performed on silica gel (60-mesh, Merck).

Bromination of (1S,4S,5S,8S)-tetrabromo-1,2,3,4,5,6,7,8-octahydronaphthalene (7)

To tetrabromide **7** (1.0 g, 2.2 mmol) was added dropwise and over 1.5 h bromine (0.88 g, 5.5 mmol) at 120 °C while stirring. The resulting solution was stirred at the same temperature for additional 30 min. After cooling to room temperature, the residue was analysed by NMR spectrocopy. (For the separation of these compounds see below)

1,4-Dibromonaphthalene (**8**)	177 mg,	28 %
1,5-Dibromonaphthalene (**9**)	133 mg,	21 %
1,4,6-Tribromonaphthalene (**10**)	105 mg,	13 %
1,4,5-Tribromonaphthalene (**11**)	73 mg,	9 %
Hexabromide (**12**)	54 mg,	4 %
Hexabromide (**13**)	80 mg,	6 %

Thermal Reaction of Tetrabromide (7)

To a two necked round-bottomed flask (20 ml) equipped with reflux condenser was added tetrabromide **7** (1.0 g, 2.21 mmol) and heated at 150 °C for 5 days. The sublimated product (280 mg, 97%) was characterized as naphthalene (**14**).

Bromination of Naphthalene (14)

To naphthalene (3.0 g, 23.4 mmol) was added dropwise over 40 min. bromine (3.93 g, 24.54 mmol) at 120 °C while stirring. The resulting solution was stirred at the same temperature for additional 1h. After cooling to room temperature, the mixture was distilled at 143-145 °C (20 mm Hg) yielding 1-bromonaphthalene (**15**) (4.35 g, 90 %); δ_H (200 MHz, $CDCl_3$) 8.33 (1H, bd, *J* 8.4 Hz, H8) 7.90-7.32 (6H, m, ArH); δ_C (50 MHz, $CDCl_3$) 135.19, 132.56, 130.49, 128.90, 128.52, 127.92, 127.68, 127.28, 126.76, 123.43.

Bromination of 1-Bromonaphthalene (15)

To 1-bromonaphthalene (**15**) (2.07 g, 10.0 mmol) was added dropwise over 40 min. bromine (2.4 g, 15 mmol) at 120 °C while stirring under reflux condenser. After completion of the addition, the resulting solution was stirred at 120 °C for additional 1h and cooled to room temperature. The residue was chromatographed over silica gel (10 g). Elution with hexane gave a mixture of 1,4-dibromonaphthalene (**8**) and 1,5-dibromonaphthalene (**9**) which was crystallized from hexane. The formed crystals were identified as 1.4-dibromonaphthalene (**8**) (0.5 g, pale yellow crystals, 1.6 g mixture, total yield 73 %, m.p. 80 °C (Lit m.p. 81-82 °C[9]); δ_H (200 MHz, $CDCl_3$) 8.26-7.61 (4H, AA'BB' system, ArH), 7.61 (2H, s, ArH); δ_C (50 MHz, $CDCl_3$) 133.37, 130.54, 128.65, 128.25, 123.09.

After filtration of **8** the solvent was evaporated, the residue was crystallized from ethanol and 1,5-dibromonaphthalene (**9**) obtained as the sole material (150 mg, pale yellow crystals, 450 mg mixture, total yield 21 %), m.p. 128-129 °C, (Lit. m.p. 131°C[9]); δ_H (200 MHz, $CDCl_3$) 8.23 (2H, d, *J* 8.1 Hz, ArH), 7.83 (2H, d, *J* 7.0 Hz, ArH), 7.41 (2H, t, ArH); δ_C (50 MHz, $CDCl_3$) 133.51, 131.38, 127.89, 127.79, 123.52.

Bromination of 1,4-Dibromonaphthalene (8) at 120 °C

To 1,4-dibromonaphthalene (**2**) (300 mg, 1.05 mmol) was added dropwise and over 30 min. bromine (5.5 g, 34.4 mmol) at 120 °C while stirring. The resulting solution was stirred at 120 °C for additional 3h. After cooling to room temperature, unreacted bromine was evaporated at the reduced pressure at 30 °C. The residue was submitted to silica gel (90 g) chromatography. Elution with hexane gave five products.

The first fraction: **1,4,6-Tribromonaphthalene (10)** (80 mg, 21 %), yellow crystals, m.p. 86-87 °C from methylene chloride/hexane (Lit. m.p. 86-87 °C[3]); δ_H (200 MHz, $CDCl_3$) 8.36 (1H, d, *J* 1.9 Hz, H5), 8.04 (1H, d, *J* 9.0, H8), 7.65 (1H, dd, H7) 7.58 (2H, m, H2, H3); δ_C (50 MHz, $CDCl_3$) 134.29, 132.02, 131.91, 131.53, 130.88, 130.36, 129.98, 123.47, 122.95, 121.67.

The second fraction: **1,4,5-Tribromonaphthalene (11)**, (50 mg, 13 %).yellow crystals, m.p. 80-81 °C from methylene chloride/hexane (Lit. m.p. 85-86 °C[7]); δ_H (200 MHz, $CDCl_3$) 8.36, (1H, dd, *J* 8.5, 1.2 Hz, H8) 8.01 (1H, dd, *J* 7.5 Hz, H6) 7.77 (1H, d, *J* 8.1 Hz, ,H2 or H3) 7.60 (1H, d, H2 or H3), 7.38 1H, dd, H7); δ_C (50 MHz, $CDCl_3$) 138.29, 137.24, 137.16, 137.02, 132.76, 130.94, 129.63, 125.61, 122.17, 121.53.

The third fraction: **(1R,2S,3R,4S-tetrabromo-1,2,3,4-tetrahydronaphthalene (17)** (20 mg, 3 %) colorless crystals from THF /methylen chloride, m.p. 132-133 °C; [Found: C, 78.95; H, 1.06. $C_{10}H_6Br_6$ requires C, 79.17; H 1.0 %]; ν_{max} (KBr) 2975, 2960, 2940, 1427, 1340, 1280, 1270, 1120, 902 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.49, (2H, s, ArH) 5.52 (2H, A part of

AA'BB' system, H1 and H4), 5.26 (2H, B part of AA'BB' system, H2 and H3); δ_C (50 MHz, $CDCl_3$) 135.80, 135.53, 125.59, 54.86, 50.96.

The fourth fraction: **(1R,2R,3R,4R-tetrabromo-1,2,3,4-tetrahydronaphthalene (12)**: (127 mg, 20 %) colorless crystals from methylene chloride/hexane, decomp. p. 165-172 °; [Found: C, 78.28; H, 1.06. $C_{10}H_6Br_6$ requires C, 79.17; H, 1.0%]; ν_{max} (KBr) 2965, 2935, 2920, 1552, 1430, 1340, 1240, 1187, 1170, 1130, 1024, 920, 800 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.47 (2H, s, ArH), 5.79 (2H, AA'BB' system, H1 and H4), 5.02 (2H, B part of AA'BB' system, H2 and H3); δ_C (50 MHz, $CDCl_3$) 136.08, 135.80, 124.98, 58.02, 52.72.

Fifth fraction: **(1R,2R,3R,4S-tetrabromo-1,2,3,4-tetrahydronaphthalene (13)**: (89 mg, 13 %) colorless crystals from methylene chloride/hexane, decomp. p. 165-172 °C; [Found: C, 79.01; H, 1.07. $C_{10}H_6Br_6$ requires C, 79.17; H, 1.0%]; ν_{max} (KBr) 3040, 2950, 2920, 1975, 1970, 1437, 1333, 1260, 1190, 1140, 1030, 908, 828, 820; δ_H (200 MHz, $CDCl_3$) 7.49-7.48 (2H, m, ArH), 5.81 (1H, d, *J* 4.2 Hz, H1), 5.63 (1H, d, *J* 3.0 Hz, H4), 5.23 (1H, dd, *J* 11.3 Hz, H2) 4.26 (1H, dd, H3); δ_C 50 MHz, $CDCl_3$) 137.53, 136.39, 135.84, 135.11, 125.59, 123.12, 57.83, 54.77, 53.05, 51.95.

Photobromination of 1,4-Dibromonaphthalene (8) without Solvent at 30 °C

To 1,4-Dibromonaphthalene (**8**) (200 mg, 0.70 mmol) was added dropwise and over 30 min. bromine (4.0 g, 25 mmol) at 30 °C while the reaction flask was irradiated with two 150 W sun lamps. The resulting solution was photolyzed for additional 3 h while the temperature was controlled by an internal thermometer. The unreacted bromine was evaporated at reduced pressure and 20 °C. The residue was submitted to column chromatograpy (silica gel, 90 g). Elution with hexane gave four products in the following order.

The first fraction: **17** (59 mg, 14%)

The second fraction: **(1R,2S,3S,4R)-tetrabromo-1,2,3,4-tetrahydronaphthalene (16)** (34 mg, 8%), colorless crystals from THF/methylene chloride, decomp. p. 125-128 °C. [Found: C, 78.61; H, 1.01. $C_{10}H_6Br_6$ requires C, 79.17; H, 1.0%]; ν_{max} (KBr) 3040, 2980, 1920, 1885, 1870, 1420, 1308, 1220, 1195, 1168, 1120, 1100, 895, 810 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.55 (2H, s, ArH) 6.04, (2H, A-part of AA'BB' system, H1 and H4), 5.44 (2H, B part of AA'BB' system, H2 and H3); δ_C (50 MHz, $CDCl_3$), 135.97, 133.79, 126.93, 45.90, 45.04.

The third fraction: **12** (59 mg, 14%)

The fourth fraction : **13** (229 mg, 54%)

Photobromination of 1,4-Dibromonaphthalene (8) in CCl_4 at 30 °C

To 1,4-Dibromonaphthalene (**2**) (200 mg, 0.70 mmol) in CCl_4 (2 ml) was added dropwise and over 10 min. bromine (336 mg, 2.1 mmol) in CCl_4 (1 ml) at 30 °C while the reaction flask was irradiated with two 150 W sun lamps. The resulting solution was photolyzed for additional 2h while the temperature was controlled by an internal thermometer. After removal of the unreacted bromine and solvent at reduced pressure and 20 °C, the residue was analyzed by ^{1}H-NMR spectral measurements.

Hexabromide **17**	394 mg,	93 %
Hexabromide **12**	21 mg,	5 %
Hexabromide **13**	4 mg,	1 %

General Procedure for Elimination of hexabromides (12), (13) and (17)

A solution of either pure hexabromides (**12, 13, 17**) or a mixture consisting of either (**12** and **13**) and (**17**) (1.1 g, 1.82 mmol) in dry tetrahydrofuran (10 ml) was added dropwise to a stirring solution of potassium-tert-butoxide (1.0 g, 8.9

mmol) in dry tetrahydrofuran during 20 min at 10 °C. The mixture was stirred overnight at r.t. and quenched with water. The mixture was extracted with ether, dried ($MgSO_4$), and concentrated at reduced pressure. Crystallization from methylene chloride/hexane afforded 350 mg 1,4,6,7-tetrabromonaphthalene **22** as colorless crystals and 95 mg mixture, (total yield 55 %) m.p. 168-169 °C; [Found: C, 27.33; H, 0.93. $C_{10}H_4Br_4$ requires C, 27.06; H, 0.91%]; ν_{max} (KBr) 3090, 3060, 3040, 1558, 1454, 1400, 1290, 1280, 1245, 1190, 1170, 1112, 965 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.50 (2H, s, ArH), 7.63 (2H, s, ArH); δ_C (50 MHz, $CDCl_3$) 132.93, 132.77, 131.74, 125.94, 121.46.

After filtration of **22**, the solvent was evaporated and the residue was crystallized from methylene chloride/hexane and 100 mg 1,4,6-tribromonaphthalene (**10**) was obtained as yellow crystals and 144 mg mixture (total yield of 37 %). m.p. 86-87 °C (Lit. m.p. 86-87 °C[7]).

Thermal reaction of hexabromides (12), (13) and (17)

A solution of a mixture consisting of **12, 13** and **17** (ca. 200 mg) in a sealed glas-tube was heated at 165-170 °C for 1h. The formation of elemental bromine was observed. ^{1}H-NMR analysis of the reaction mixture indicated the formation of **8** and **10** in a ration of 74:26.

Photobromination of Naphthalene in CCl_4 at 30 °C

To the solution of naphthalene (4 g, 31.25 mmol) in CCl_4 (25 ml) was added dropwise and over 3 h bromine (5 g, 31.25 mmol) in CCl_4 (10 ml) at 30 °C while the reaction flask was irradiated with two 150 W sun lamps. The resulting solution was photolyzed for additional 7 h while the temperature was controlled by an internal thermometer. After evaporation of the unreacted bromine at reduced pressure at 20 °C, the residue was crystallized from methylene chloride/hexane to give **24**, (2.05 g crystals, 0.4 g from silica gel column (Total yield 35%) colorless crystals, dec.p. 103-105°C; [Found: C, 27.23; H, 1.42. $C_{10}H_6Br_4$ requires C, 26.94; H, 1.36%] ν_{max} (KBr) 3030, 2980, 2970, 1595, 1570, 1490, 1448, 1325, 1306, 1232, 1198, 1148, 1108, 880 cm^{-1}; δ_C (200 MHz, $CDCl_3$) 7.64-7.40 (4H, AA'BB' system, ArH), 5.72 (2H, A part of AA'BB' system, H1 and H4), 5.02, (2H, B part of AA'BB' system, H2 and H3); δ_C (50 MHz, $CDCl_3$) 133.38, 130.59, 130.17, 54.54, 50.71.

After the filtration of **24**, the residue subjected to silica gel (130 g) chromatography eluting with hexane. The first fraction consisting of a mixture of naphthalene and 1-bromonaphthalene (**15**) was analyzed by ^{1}H-NMR: Unreacted naphthalene 2.6 g, 1-bromonaphthalene (**15**) 1.62 g (25 %).

The second fraction : tetrabromide **24** (0.4 g, total 2.45 g, 35 %)

The third fraction: **(1R,2S,3R,4S)-Tetrabromo-1,2,3,4-tetrahydronaphthalene (25)**: (210 mg, 3 %), colorless crystals, m.p. 95-96°C from methylene chloride/hexane; [Found: C, 27.02; H, 1.44. $C_{10}H_6Br_4$ requires C, 26.94, H;1.36%]; ν_{max} (KBr) 2990, 2938, 2910, 1482, 1450, 1250, 1238, 1200, 1180, 1150, 1132, 1100, 880, 765 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.47-7.32, (4H, AA'BB' system, ArH), 5.63 (2H, A part of AA'BB' system, H1 and H4), 5.10 (2H, B part of AA'BB' system, H2 and H3); δ_C (50 MHz, $CDCl_3$) 134.75, 132.92, 131.54, 56.61, 53.31.

Fourth fraction: **(1S,2S,3S,4R)-Tetrabromo-1,2,3,4-tetrahydronaphthalene (23):** (420 mg, 6%) m.p. 111-112°C, colourless crystals from methylene chloride/hexane; [Found: C, 27.38; H, 1.41. $C_{10}H_6Br_4$ requires C, 26.94; H, 1.36%); ν_{max} (KBr) 3060, 2978, 2940, 1482, 1448, 1330, 1252, 1212, 1188, 1160, 1135, 1093, 1029, 951, 880, 802, 770; δ_H (200

MHz, $CDCl_3$) 7.57-7.21 (4H, m, ArH), 5.78 (1H, d, *J* 7.1 Hz, H1), 5.53 (1H, d, *J* 3.0 Hz, H4), 5.13 (1H, dd, *J* 11.3 Hz, H2), 4.45 (1H, dd, H3); δ_C (50 MHz, $CDCl_3$) 135.40, 134.08, 131.80, 130.65, 129.83, 128.69, 57.99, 54.96, 54.30, 53.08.

Elimination of Tetrabromide (24)

A solution of **24** (1.11 g, 2.48 mmol) in dry tetrahydrofuran (10 ml) was added dropwise to a stirring solution of potassium-tert-butoxide (1.10 g, 9.9 mmol) in dry tetrahydrofuran (5 ml) during 20 min at 10°C. The mixture was stirred overnight at r.t. and quenched with water. The mixture was extracted with ether, dried ($MgSO_4$), and concentrated at reduced pressure. The residue was chromatographed on silica gel (5 g) eluting with hexane. Crystallization from methylene chloride/hexane gave 1,3-Dibromonaphthalene (**25**): (620 mg, 87%):, m.p.62 °C colorless crystals from methylene chloride/hexane, (Lit. m.p. 64 °C[9]); δ_H (200 MHz, $CDCl_3$) 8.17 (1H, bd, *J* 8.4 Hz, H8), 7.95 (1H, m, H4), 7.88 (1H, m, H2), 7.74-7.49 (3H, m, H5, H6 and H7) δ_C (50 MHz, $CDCl_3$) 135.57, 132.98, 131.07, 130.38, 128.23, 128.13, 127.94, 127.68, 124.01, 119.38.

Crystallography: Data were collected on a Enraf-Nonius CAD-4 diffractometer (Enraf-Nonius, 1993). The structures were solved by using direct method (SIR88)[21] and refined by full matrix least-squares.[22] Program used for molecular graphics was PIATON-98.[23,24] Crystallographic data are deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements: The authors are indebted to the Department of Chemistry and Atatürk University for financial support and State Planning Organization of Turkey (DPT) for purchasing a 200 MHz NMR (Atatürk University) and CAD-4 Diffractometer (Hacettepe University) under Grant DPT/TBAG1.

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