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MEHMET EMİN ŞENGÜL

DEMET DEMİRCİ GÜLTEKİN

SELÇUK EŞSİZ

ARİF DAŞTAN

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Bromination of Tetrachlorobenzobarrelene: Polyhalogenated Benzobicyclics

Mehmet Emin ŞENGÜL, Demet DEMİRCİ GÜLTEKİN, Selçuk EŞSİZ and Arif DAŞTAN*
Department of Chemistry, Atatürk University, 25240 Erzurum-TURKEY
e-mail: adastan@atauni.edu.tr

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The low and high temperature bromination reaction of tetrachlorobenzobarrelene was studied and the possible role of a neighboring group in rearrangements was investigated. New polyhalogenated benzobicyclic compounds were synthesized. All compounds were characterized properly using NMR spectroscopy.

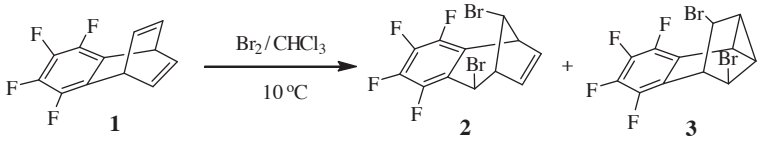
Key Words: Benzobarrelene, bromination, Wagner-Meerwein rearrangement, polyhalogenides.

Introduction

The addition of bromine to the carbon-carbon double bond is one of the best known reactions typical of unsaturated compounds.[1] In general, the reaction is stereoselective and leads to *trans*-1,2-dibromides via the 3-membered bromonium intermediate.[2] The bromination of unsaturated bicyclic systems with molecular bromine is generally complicated.[3] For this reason, bromination of bridged olefins has attracted a good deal of attention for a long time. In addition to mechanical aspect, highly brominated compounds have numerous industrial applications as pesticides, plastics, fire-retardants, and pharmaceutical chemicals,[4] and play an important role as key compounds for the synthesis of other derivatives.[5]

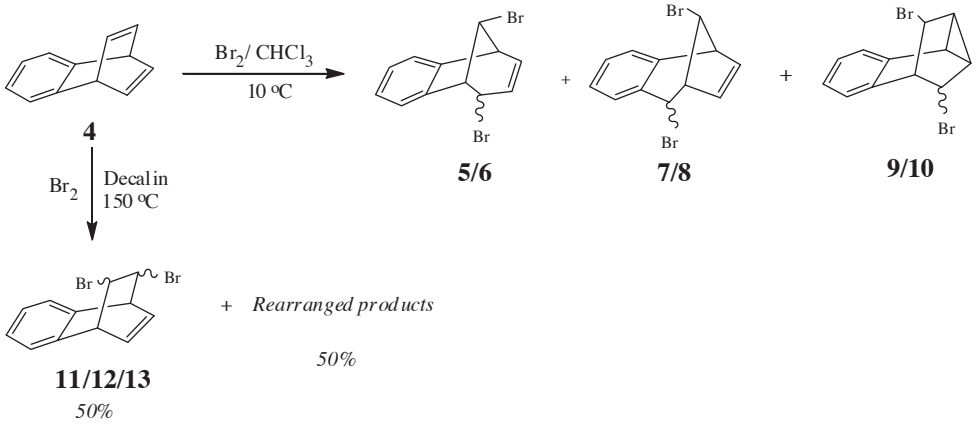
Some interest has been focused on the halogenation of benzobarrelene and its derivatives.[6] Barkhash et al.[6c] have reported previously the bromination of tetrafluorobenzobarrelene **1** and isolated only 2 compounds: **2** and **3** (Scheme 1).

*Corresponding author



Scheme 1

In a previous study we showed that bromination of benzobarrelene **4** at low temperature results in the formation of rearranged products **5-10**[6a] in quantitative yield. However, when the bromination reaction of this molecule was carried out at 150 °C, the *non*-rearranged isomeric products **11-13** were formed in 50% yield along with the rearranged products **5-10**. We also found that there was competition between the radical and ionic bromination at high temperature (Scheme 2).

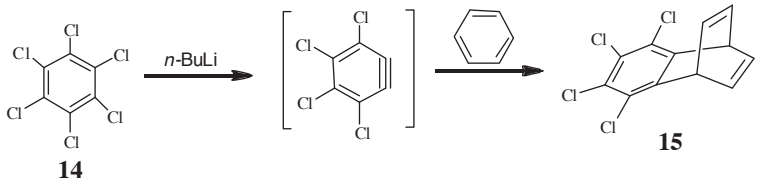


Scheme 2

Results and Discussion

In this paper, we discuss the bromination reactions of compound **15** having 4 chlorine atoms in the benzene ring and report the synthesis of poly-halogenated benzobicyclics.

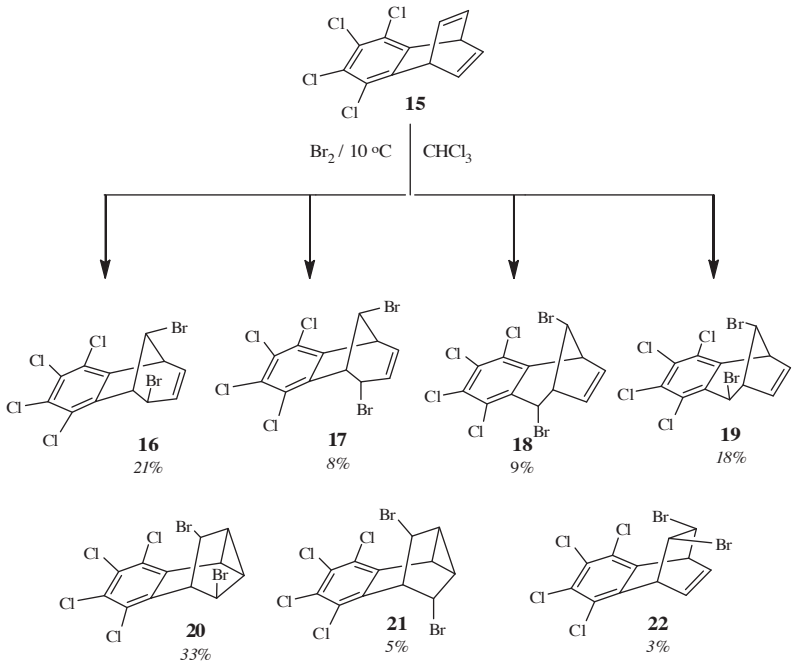
The starting material, tetrachlorobenzobarrelene (**15**), was synthesized using a procedure described in the literature[7] (Scheme 3).



Scheme 3

The electrophilic addition of bromine to **15** was carried out in chloroform solution at 10 °C. The ^{1}H-NMR spectral studies of the crude product revealed the formation of 6 isomeric rearranged products **16-21**

beside *non*-rearranged product **22**. The mixture was separated by silica gel column chromatography as shown in Scheme 4.



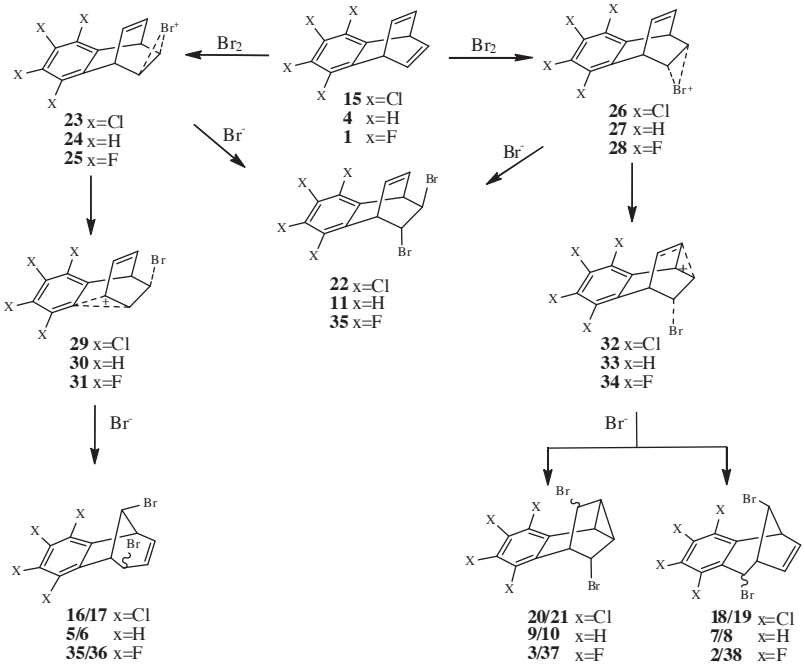
Scheme 4

The proposed mechanism for the formation of the products is outlined in Scheme 5. According to the mechanism, compounds **18-21** and **22** are formed via *endo*-bromonium ion **26**. *exo*-Bromonium ion **23** is responsible for the formation of **16**, **17**, and **22**.

In the bromination of benzobarrelene **4**, it was observed that the ratio of products via *exo*-bromonium ion to products via *endo*-bromonium ion is approximately 3:1. This is evidently due to the higher rate of the formation of ion **24**, which is stabilized on account of the π participation of the aromatic ring (ion **30**);[6a] such participation is significantly more effective than the participation of the double bond, as in ion **33**. In the case of **15** we found that the ratio of the products **16/17** formed from *exo* ion **23** and the products **18-21** formed from *endo* ion **26** amounts to $\sim$3:7 (Table). These differences are due to fact that the intermediate **29** is less favorable because of the electronegative chlorine atoms in the benzene ring in molecule **15**. Barkhash and co-workers reported that only products **2** and **3** were formed via *endo*-bromonium ion **28** in the bromination of **1**. Our study supports the mentioned postulate, taking into account that in the case of a more electronegative fluorine atom in the benzene ring the formation of *exo*-bromonium ion **25** is not preferred at all.

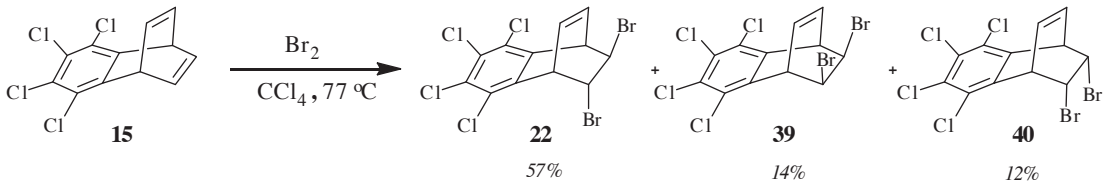
Table. Product rations formed via *exo*-and *endo*-bromonium ions.

Benzobarrelene derivatives	Product ration formed via *endo*-bromonium ions	Product ration formed via *exo*-bromonium ions
4	$\sim$ 25	$\sim$ 75
15	$\sim$ 69	$\sim$ 31
1	$\sim$ 100	$\sim$ 0



Scheme 5

In the experiments following we aimed to minimize the formation of rearranged products **16-21** and obtain *non*-rearranged products in high yield. For this reason, the reaction was carried out at higher temperature and the *non*-rearranged products **22**, **39**, and **40** were obtained in 83% total yield (Scheme 6).



Scheme 6

The results of the high temperature bromination demonstrate that the tendency of the chlorine functionalized benzobarrelene system like **15** to undergo Wagner-Meerwein rearrangement is less than that found in the *non*-substituted benzobarrelene system like **4**. In the case of benzobarrelene **4**, a much higher temperature (150 °C) was applied to prevent the skeletal rearrangement[6a] resulting in little success. However, for **15**, 77 °C was sufficient to prevent skeletal rearrangement. At this temperature, small amounts of the rearranged products were detected, whereas from the bromination of benzobarrelene **4** at 77 °C *non*-rearranged products were obtained only in 15% yields in our unpublished results.

The structures of these compounds were elucidated on the basis of ^{1}H- and ^{13}C-NMR spectral data, extensive double resonance experiments, and by comparison of some spectral data of related systems reported in the literature.[6,8]

Experimental

General: Melting points are uncorrected. Infrared spectra were obtained from KBr pellets on a regular instrument. The ^{1}H- and ^{13}C-NMR spectra were recorded on 400 (100)-MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. All substances reported in this paper are in their racemic form.

Caution: It has been reported[9] that of 3 laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, 2 later developed similar pulmonary disorders, which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of dibromide derived from benzonorbornadiene there is no report in the literature about the toxicological effect. However, we recommend that the compounds be handled only with extreme caution. Carbon tetrachloride is also toxic. Therefore, personnel and environmental precautions must be taken.

1. Synthesis of tetrachlorobenzobarrelene (15). The starting material, tetrachlorobenzobarrelene (**15**), was synthesized using a procedure described in the literature.[7] ^{1}H-NMR (400 MHz, $CDCl_3$): 6.94-6.90 (AA'BB' system, 4H, H_2, H_3, H_9 and H_{10}), 5.44 (m, 2H, H_1 and H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): 146.54, 139.85, 128.05, 126.53, 47.27.

2. Bromination of tetrachlorobenzobarrelene (15) at 10 °C:

To a magnetically stirred solution of tetrachlorobenzobarrelene (**15**) (584 mg, 2.0 mmol) in 15 mL of dry chloroform at 10 °C was added dropwise a solution of bromine (320 mg, 2.0 mmol) in 5 mL of chloroform over 5 min. After completion of the addition, the solution was allowed to warm to 20 °C. The solvent was removed under reduced pressure. The residue was chromatographed on silica gel (100 g), eluting with hexane.

The first fraction: *(1R(S),4S(R),9R(S),10R(S))-9,10-dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethano-naphthalene* (**22**): (27 mg, 3%, mp 131-132 °C colorless crystals from methylene chloride/$n-$hexane (1:1). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.70 (m, 2H, H_2 and H_3), 4.77 (m, 1H, H_9 or H_{10}), 4.73 (m, 1H, H_9 or H_{10}), 4.23 (m, 1H, H_1 or H_4), 3.99 (m, 1H, H_1 or H_4). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.26, 138.21, 134.86, 133.88, 131.68, 131.44, 130.34, 128.06, 52.61, 52.16, 46.88, 46.15. IR (KBr, cm^{-1}): 3068, 2999, 2926, 1378, 1269, 1220, 1166, 808, 712. Found: C, 32.01; H, 1.37; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The second fraction: *(5S(R),8S(R),9S(R),10R(S))-9,10-dibromo-1,2,3,4-tetrachloro-8,9-dihydro-5H-5,8-methanobenzo[a][7]annulen* (**18**): (82 mg, 9%, methylene chloride/$n-$hexane (1:1) mp 159-161 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.43 (dd, $J_{6,7}$=6.0 Hz, $J_{5,6}$=3.4 Hz, 1H, H_6), 6.18 (dd, $J_{6,7}$=6.0 Hz, $J_{7,8}$=3.1 Hz, 1H, H_7), 5.39 (d, $J_{8,9}$=5.8 Hz, 1H, H_9), 4.75 (t, $J_{5,10}$=$J_{8,10}$=4.5 Hz, 1H, H_{10}), 4.18 (dd, $J_{5,10}$=4.5 Hz, $J_{5,6}$=3.4 Hz, 1H, H_5), 3.41 (ddd, $J_{8,9}$=5.8 Hz, $J_{8,10}$=4.5 Hz, $J_{7,8}$=3.1 Hz, 1H, H_8). ^{13}C-NMR (100 MHz, $CDCl_3$): 136.95, 136.61(2C), 134.84, 133.72, 133.01, 132.94, 130.76, 52.73, 49.68, 47.98, 45.57. IR (KBr, cm^{-1}): 3048, 2978, 2930, 1374, 1242, 1168, 884, 865, 811,732. Found: C, 32.11; H, 1.31; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The third fraction: *(5S(R),6S(R),9S(R),10S(R))-6,10-dibromo-1,2,3,4-tetrachloro-6,9-dihydro-5H-5,9-methanobenzo[a][7]annulen* (**17**): (72 mg, 8%, methylene chloride/$n-$hexane (1:1) mp 176-177 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.08 (bdd, $J_{7,8}$=9.5 Hz, $J_{8,9}$=6.4 Hz, 1H, H_8), 5.69 (bdd, $J_{7,8}$=9.5 Hz, $J_{6,7}$=2.2 Hz, 1H,

H_7), 5.31 (bdd, $J_{5,6}$=4.8 Hz, $J_{6,7}$=2.2 Hz, 1H, H_6), 4.63 (dt, $J_{5,10}$=$J_{9,10}$=4.5 Hz, $J_{8,10}$=1.2 Hz, 1H, H_{10}), 4.00 (m, 1H, H_5), 3.73 (bdd, $J_{8,9}$=6.4 Hz, $J_{9,10}$=4.5 Hz, 1H, H_9). ^{13}C-NMR (100 MHz, $CDCl_3$): 146.47, 138.47, 132.73, 132.17, 130.88, 128.68, 127.83, 126.04, 52.32, 51.97, 45.67, 45.49. IR (KBr, cm^{-1}): 3036, 2958, 2919, 1373, 1280, 1243, 1168, 874, 748. Found: C, 31.74; H, 1.34; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The fourth fraction: *1R(S),1aR(S),2R(S),8R(S)-2,8-dibromo-4,5,6,7-tetrachloro-1a,2,3,7b-tetrahydro-1H-1,3-methanocyclopropa[a]naphthalene* (**20**): (300 mg, 33%, methylene chloride/$n-$hexane (1:1) mp 162-163 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.06 (dd, $J_{3,8}$=4.7 Hz, $J_{1,8}$=2.8 Hz, 1H, H_8), 4.17 (bd, $J_{2,3}$= $J_{3,8}$=4.7 Hz, 1H, H_3), 3.70 (s, 1H, H_2), 3.06 (t, $J_{1,7b}$= $J_{1a,7b}$=7.3 Hz, 1H, H_{7b}), 2.44 (m, 1H, H_1), 2.28 (bdd, $J_{1a,7b}$= 7.3 Hz, $J_{1,1a}$=5.6 Hz, 1H, H_{1a}). ^{13}C-NMR (100 MHz, $CDCl_3$): 132.74, 132.47, 131.15, 130.75, 130.38, 129.94, 49.24, 48.41, 45.37, 27.25, 24.55, 22.63. IR (KBr, cm^{-1}): 2952, 2926, 2852, 1386, 1285, 1223, 1163, 859, 777. Found: C, 32.30; H, 1.34; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The fifth fraction: *(5S(R),6R(S),9S(R),10S(R))-6,10-dibromo-1,2,3,4-tetrachloro-6,9-dihydro-5H-5,9-methanobenzo[a][7]annulen* (**16**): (190 mg, 21%, methylene chloride/$n-$hexane (1:1) mp 175-176 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.20 (bdd, $J_{7,8}$=9.7 Hz, $J_{8,9}$=6.6 Hz, 1H, H_8), 5.76 (ddd, $J_{7,8}$=9.7 Hz, $J_{6,7}$=3.1 Hz, $J_{5,7}$=1.5 Hz, 1H, H_7), 4.74 (dt, $J_{5,10}$=$J_{9,10}$=4.3 Hz, $J_{8,10}$=0.9 Hz, 1H, H_{10}), 4.60 (dt, $J_{6,7}$=3.1 Hz, $J_{5,6}$=$J_{6,8}$=1.2 Hz, 1H, H_6), 3.99 (bdd, $J_{5,10}$=4.3 Hz, $J_{5,7}$=1.5 Hz, 1H, H_5), 3.88 (bdd, $J_{8,9}$=6.6 Hz, $J_{9,10}$=4.3 Hz, 1H, H_9). ^{13}C-NMR (100 MHz, $CDCl_3$): 147.16, 138.99, 132.69, 132.00, 129.56, 128.72, 127.98, 126.58, 50.54, 46.31, 44.84, 40.58. IR (KBr, cm^{-1}): 2961, 2919, 2846, 1373, 1247, 1160, 1139, 742, 715. Found: C, 31.71; H, 1.34; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The sixth fraction: *(5S(R),8S(R),9R(S),10R(S))-9,10-dibromo-1,2,3,4-tetrachloro-8,9-dihydro-5H-5,8 methanobenzo[a][7]annulen* (**19**): (163 mg, 18%, methylene chloride/$n-$hexane (1:1) mp 184-185 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.48 (dd, $J_{6,7}$=6.0 Hz, $J_{5,6}$=3.3 Hz, 1H, H_6), 5.97 (dd, $J_{6,7}$=6.0 Hz, $J_{7,8}$=3.2 Hz, 1H, H_7), 4.98 (dd, $J_{8,9}$=1.4 Hz, $J_{9,10}$=0.8 Hz, 1H, H_9), 4.77 (dt, $J_{5,10}$=$J_{8,10}$=4.5 Hz, $J_{9,10}$=0.8 Hz, 1H, H_{10}), 4.39 (m, 1H, H_5), 3.56 (m, 1H, H_8).^{13}C-NMR (100 MHz, $CDCl_3$): 142.99, 138.69, 135.72, 133.26, 133.23, 132.42, 132.07, 131.05, 49.35, 48.69, 46.82, 40.90. IR (KBr, cm^{-1}): 2956, 2919, 2852, 1372, 1249, 1148, 914, 888, 778. Found: C, 31.80; H, 1.35; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The seventh fraction: *(1R(S),1aR(S),2S(R),8R(S)-2,8-dibromo-4,5,6,7-tetrachloro-1a,2,3,7b-tetrahydro-1H-1,3 methanocyclopropa[a]naphthalene* (**21**): (45 mg, 5%, methylene chloride/$n-$hexane (1:1) mp 195-196 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 4.54 (bd, A_2 part of A_2X system, $J_{2,3}$= $J_{3,8}$=4.9 Hz, 2H, H_2 and H_8), 4.32 (t, X part of A_2X system, $J_{2,3}$= $J_{3,8}$=4.9 Hz, 1H, H_3), 3.23 (t, X part of A_2X system, $J_{1,7b}$= $J_{1a,7b}$=7.1 Hz, 1H, H_{7b}), 2.33 (d, A_2 part of A_2X system, $J_{1,7b}$= $J_{1a,7b}$=7.1 Hz, 2H, H_1 and H_{1a}).^{13}C-NMR (100 MHz, $CDCl_3$): 132.19, 132.16, 131.22, 130.61, 130.36, 130.26, 45.27, 43.33, 26.42, 19.96. IR (KBr, cm^{-1}): 2961, 2927, 2856, 1412, 1403, 1307, 1296, 1213, 1166, 709. Found: C, 31.68; H, 1.64; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

3. Bromination of tetrachlorobenzobarrelene (15) at 77 °C: 584 mg (2.0 mmol) of **15** was dissolved in 12 mL of carbon tetrachloride (CAUTION: toxic!) in a 25 mL flask, which was equipped with a reflux condenser. The solution was heated until the carbon tetrachloride started to reflux while being stirred magnetically. To the refluxing solution was added dropwise a hot solution of bromine (384 mg, 2.4 mmol)

in 2 mL of carbon tetrachloride over 2 min. The resulting reaction mixture was heated for 2 min at reflux temperature. The solvent was evaporated and the oily residue was chromatographed on silica gel (100 g), eluting with $n-$hexane.

The first fraction: *(1R(S),4S(R),9R(S),10R(S))-9,10-dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene* (**22**): (517 mg, 57%, mp 131-132 °C colorless crystals from methylene chloride/$n-$hexane (1:1)).

The second fraction: *(1R(S),4S(R),9R(S),10S(R))-9,10-dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene* (**39**): (127 mg, 14%, methylene chloride/$n-$hexane (1:1). mp 227-228 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.73 (m, 2H, H_2 and H_3), 4.90 (m, 2H, H_1 and H_4), 4.16 (m, 2H, H_9 and H_{10}). ^{13}C-NMR (100 MHz, $CDCl_3$): 139.36, 133.75, 131.64, 128.23, 48.74, 47.10. IR (KBr, cm^{-1}): 3070, 2996, 2969, 1375, 1293, 1196, 1160, 1003, 809, 769. Found: C, 32.11; H, 1.34; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%.

The third fraction: *(1R(S),4S(R),9S(R),10R(S))-9,10-dibromo-5,6,7,8-tetrachloro-1,4-dihydro-1,4-ethanonaphthalene* (**40**): (108 mg, 12%, methylene chloride/$n-$hexane (1:1). mp 242-243 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.57 (m, 2H, H_2 and H_3), 4.91 (m, 2H, H_1 and H_4), 4.39 (m, 2H, H_9 and H_{10}). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.88, 135.84, 131.30, 130.05, 49.01, 46.93. IR (KBr, cm^{-1}): 3059, 2989, 2908, 1377, 1238, 1218, 1195, 919, 864, 720. Found: C, 32.05; H, 1.32; requires for $C_{12}H_6Br_2Cl_4$: C, 31.90; H, 1.34%. MS (EI, 70 eV): m/z 453/451/449 (M^+, 1), 373/371 (M^+-Br, 1), 291 (M^+-2Br, 5), 267(59), 221(38), 195(58), 145(43), 128(100), 110(90), 97(63%).

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