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Tetrahedron
Tetrahedron 63 (2007) 8151–8156

High temperature bromination. Part 22: Bromination of 1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene

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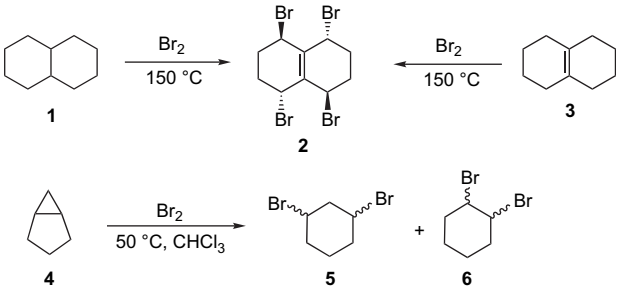
Received 9 March 2007; revised 17 May 2007; accepted 31 May 2007
Available online 6 June 2007

Abstract—The high-temperature bromination of 1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene and its carboethoxy derivative was studied. Reaction of the title compound with 1 mol of bromine in refluxing carbon tetrachloride resulted in the formation of ring-opening products. In the case of the carboethoxy derivative, bromination took place both regio- and stereospecifically at the benzylic positions, the cyclopropane ring did not undergo bond cleavage. A mechanism for the formation of the products and their dehydrobromination reactions is discussed.

1. Introduction

Although saturated hydrocarbons are readily available and extremely cheap starting materials, they cannot be used in synthetic chemistry without prior activation. The activation of alkanes can be done via halogenation using an appropriate method, which leads to the direct synthesis of haloalkanes. However, the control of regioselectivity is very difficult. We recently reported the bromination of hydrocarbons such as norbornadiene,[1] benzonorbornadiene,[2] and homobenzonorbornadiene[3] at high temperatures (80–150 °C) in nonpolar solvents (CCl_4, decalin, etc.) and noticed that mostly non-rearranged brominated products were formed; these bromination reactions proceed via a free radical mechanism. Applying this high-temperature bromination to a saturated hydrocarbon, decalin **1**[4a] as well as an unsaturated one, octalin **3**, results in bromination with remarkable regio- and stereospecificity (Scheme 1). Bromination of **1** and **3** at 150 °C gives the tetrabromide **2** as the major product.[4a]

In addition, it is well established that treatment of a cyclopropane ring with bromine produces the corresponding 1,3-dibromides.[5] For example, Lambert et al.[6] have reported that the reaction of bicyclo[3.1.0]hexane **4** with bromine results in the formation of (*cis*- and *trans*)-1,3-dibromocyclohexane **5** along with a small amount of (*cis*- and *trans*)-1,2-dibromocyclohexane **6**. However, we showed that it is possible to interrupt the opening of the cyclopropane ring using our high-temperature bromination method. An example of this being the octalin derivatives **7** and **9**, which have cyclopropane rings along with a double bond were treated with bromine, in refluxing CCl_4.[4a] The reaction produced the corresponding tetrabromides **8** and **10** with remarkable regio- and stereoselectivity where the opening of the cyclopropane ring is precluded (Scheme 2). On the other hand, simple bromination of **9** at room temperature resulted in the addition of bromine to the double bond.[4]



Scheme 1.

Inspired by these results we decided to investigate the fate of a cyclopropane ring that has active benzylic positions originating from the fused benzene ring, in high-temperature bromination reactions. For this purpose benzonorcarane **12** was chosen as a model compound. The results of this study should give an important insight into the mechanism and chemoselectivity of the reaction.

Keywords: Bromination; Dehydrobromination; Cyclopropanes; Rearrangements.
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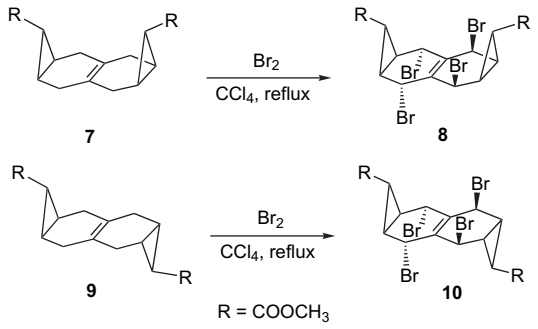
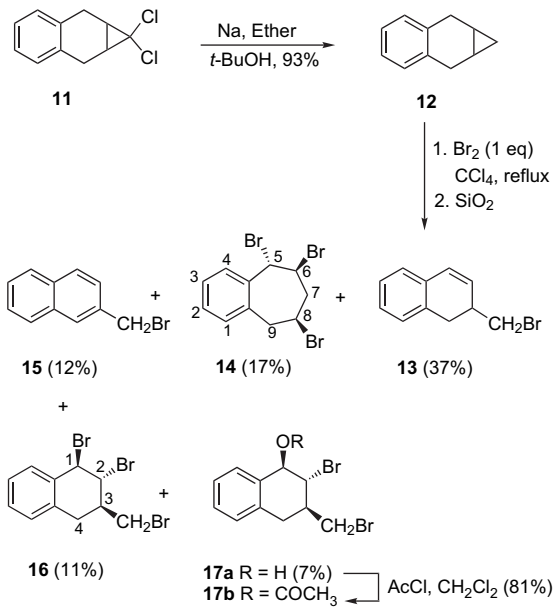
doi:10.1016/j.tet.2007.05.124



Scheme 2.

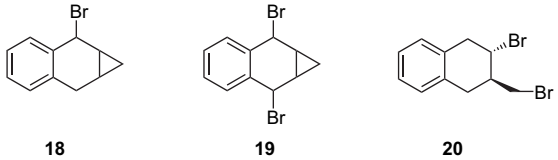
2. Results and discussions

The starting material, cyclopropa[*b*]naphthalene **12**,[7] was synthesized by addition of dichlorocarbene to the readily available 1,4-dihydronaphthalene using a phase transfer catalysis method followed by reductive dechlorination of the carbene-adduct **11**.[8] For the high-temperature bromination of **12**, bromine was directly distilled into a hot solution of **12** in refluxing carbon tetrachloride. The reaction provided a mixture consisting of five products. After repeated column chromatography, we isolated **13**–**17** in yields of 37, 17, 16, 11, and 7%, respectively (Scheme 3).



Scheme 3.

Compounds **13** and **15**[9] have been previously reported by Friedrich and Holmstead[10] in the free radical NBS α-bromination of **12**. They suggested that α-bromination products **18** and **19** are not stable under the reaction conditions and undergo rearrangement to the thermodynamically more stable bromides **13** and **15** via an ion-pair type mechanism upon standing or heating.



Shea and Skell[11] studied the photobromination of alkylcyclopropanes and showed that the first bromine radical attacks the least substituted carbon atom, with the second one going to the most substituted carbon atom. According to this mechanism, the monobromide **13** may arise from the unsymmetrical addition of bromine to **12** to give **20**, which can undergo a hydrogen bromide elimination to form **13**. The formation of **16** can be reasonably explained by addition of bromine to the double bond in **13**. Independently, pure **13** was treated with bromine under the same reaction conditions and only the tribromide **16** was obtained.

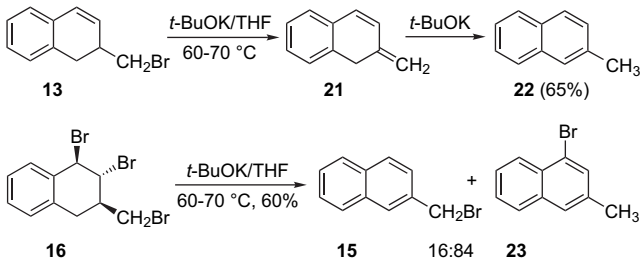
We assume that the addition of bromine to the double bond in **13** is a trans-addition. Two bromine atoms attached to the C-1 and C-2 carbon atoms in **16** can be either in axial–axial or equatorial–equatorial conformations. Wiberg calculated the energies of diaxial, axial–equatorial, and diequatorial 1,2-dibromocyclohexanes using the hybrid density functional methods B3LYP and B3P86 as well as MP2 and QCISD and the 6-311G* and 6-311+G(2df,p) basis sets. In all cases the axial–axial conformer was found to have the lowest energy by about 1.11–1.54 kcal/mol.[12] One explanation for the differences in energy between the conformers is that they result from electrostatic interactions between the C–Br dipoles. We have calculated the heat of formation energies for the two conformers of **16** using AM1 geometry optimization and found, as predicted, that the axial–axial conformer has the lowest heat of formation energy by about 1.3 kcal/mol. In the axial–axial conformation, the dihedral angle between the protons H_1 and H_2 is about 78°. The observed broad singlet resonance for H-1 proton is in agreement with this suggested trans-configuration as well as with the *aa*-conformation. The fact that the H-2 also resonates as a broad singlet, can be explained only with the trans-configuration of the bromomethylene group. In that case, the dihedral angle between the protons H-2 and H-3 is calculated to be 65°, which also is in agreement with the observed vicinal coupling constant $J_{23} \leq 1$ Hz in the ^{1}H NMR spectrum.

The hydrolysis product **17a** was formed during column chromatography. The alcohol **17a** was converted to its acetate **17b** for further characterization. The ^{1}H NMR spectrum of the alcohol displayed a doublet (J=9.2 Hz) at 5.01 ppm for the alkoxy proton H_1 and a doublet of doublets (J=11.2 and 9.2 Hz) at 4.23 ppm for the proton H_2. These large couplings in the cyclohexane ring can be observed only in the axial–axial orientation (*trans*-configuration) of the relevant protons. This finding strongly supports the *trans–trans* configuration of the substituents.

The formation of the seven-membered ring **14** can arise either from the 1,3-addition of bromine to the internal double bond of the initially formed monobromide **18** or from the addition of bromine to the cyclopropane in **12** followed by bromination of one of the benzylic carbons.

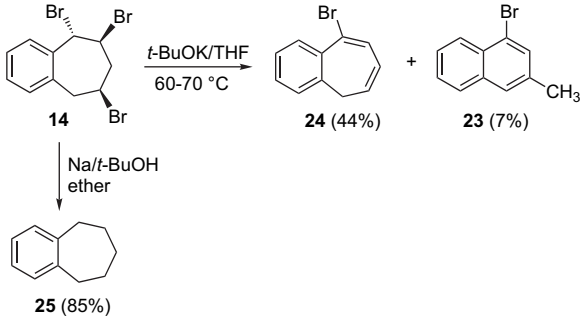
For further structural characterization of the isolated compounds, **13** and **16**, they were subjected to a base-promoted elimination reaction. The monobromide **13** gave the 2-methylnaphthalene (**22**) as the sole product in 65% yield (Scheme 4). The elimination of hydrogen bromide from **13** gives **21**,

which undergoes double bond isomerization to form **22**. Due to the structural similarity between the compounds **13** and **16** we assume that the elimination reaction of **16** follows a similar pathway and produces **15** and **23**[5c,13] in a ratio of 16:84.



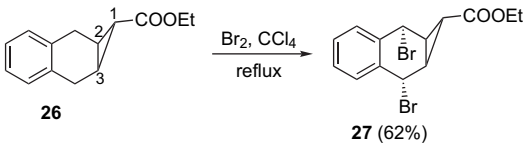
Scheme 4.

The structure of the tribromide **14** was determined by NMR and extensive double resonance experiments. ^{13}C NMR data were consistent with the proposed structure showing five aliphatic and six aromatic carbons. Chemical proof for the structure was obtained by treatment of **14** with sodium and *tert*-butyl alcohol to give benzo[*a*]cycloheptene **25**[14] (Scheme 5). Furthermore, the tribromide **14** was subjected to dehydrobromination with potassium *tert*-butoxide to give two products. The structure of the major product (44%) was shown by spectroscopic methods to be **24**. The dehydrobromination product **24** was accompanied by a small amount (7%) of the ring-constricted product **23**.



Scheme 5.

The high-temperature bromination of **12** did not show any regio- and stereoselectivity as observed for decalin and its derivatives. This is probably due to the lack of a carbonyl group bound to the cyclopropane ring, which suppress the cyclopropane bond cleavage leading to the ring-opening products. Hoffmann and Günther[15] explained this phenomenon on the basis of HOMO and LUMO interactions between the cyclopropane ring and its substituents. The dominant interaction is assumed to be between the cyclopropane 3E' Walsh-type orbital and the π^* orbital on the substituent, which causes a shortening of the distal bond between (C-2 and C-3) and stabilization of this bond. In order to see the effect of a carbonyl group on the product distribution we synthesized the *exo*-ester **26**[4b,16] and subjected it to the high-temperature bromination reaction. The reaction of **26** with bromine, in refluxing carbon tetrachloride, yielded the corresponding dibromide **27** as the sole product in 62% yield (Scheme 6).



Scheme 6.

The dibromide **27** was also observed in the free radical NBS α-bromination of **26** but information about the stereochemistry of the bromine atoms in this case was not given.[17] The proton and carbon NMR spectra show a plane-symmetry in the molecule. A nine-line ^{13}C NMR spectrum is in agreement with structure **27**. The configuration of bromine atoms was determined by a NOE experiment. Irradiation at the resonance frequency of the benzylic protons (δ 5.66) causes enhancement at the resonance signals of the endo-cyclopropane proton resonating at δ 1.46 as well as of the other cyclopropane protons resonating at δ 2.75. This NOE experiment clearly indicates that the bromines are in a cis-configuration and are located in an anti-position with respect to the cyclopropane ring in **27**.

In conclusion, the high-temperature bromination of **12** resulted in the formation of ring-opening products, and the regio- and stereoselectivity was not observed. In the case of **26**, the high-temperature bromination proceeded regio- and stereospecifically at the benzylic positions. The carbonyl group bound to the cyclopropane ring in **26** prevents the opening of the ring.

3. Experimental

3.1. General

Melting points were determined on a Büchi model 530 apparatus and are uncorrected. Infrared spectra were recorded on a Mattson model 1000 FTIR and Shimadzu model 8300 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)-MHz spectrometers. Mass spectra (EI) were recorded at 70 eV as *m*/*z*. Column chromatography was performed on silica gel 60 (70–230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. Elemental analysis was determined on a Leco CHNS-932 instrument.

3.2. 1,1-Dichloro-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene (11)

The dichlorocyclopropane compound was prepared in 70% yield as described in the literature.[8b]

3.3. 1a,2,7,7a-Tetrahydro-1*H*-cyclopropa[*b*]naphthalene (12)

Metallic sodium (10.9 g, 474 mmol) was cut into small pieces and combined with 80 mL of anhydrous ether. This was magnetically stirred under nitrogen atmosphere while a mixture of the dichlorocarbene-adduct **11** (10.0 g, 46.9 mmol), *tert*-butanol (34.3 g, 464 mmol), and ether (50 mL) was added dropwise over a period of 2 h. The reaction mixture was stirred for additional 24 h at room temperature and methanol (20 mL) and then water (40 mL) was

added dropwise. The mixture was diluted with water (50 mL) and the aqueous solution was extracted with ether (3×100 mL), washed with water (2×50 mL), and dried over $CaCl_2$. After removal of the solvent, 6.29 g (93%) of **12** was obtained as a crystalline solid, mp 31–32 °C (lit.[7] 31–32 °C). Comparison of the spectral data of this compound with those reported in the literature[7] was in full agreement.

3.4. Bromination of 1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene (12) at 77 °C

Two grams (13.8 mmol) of **12** was dissolved in 30 mL of carbon tetrachloride in a 100 mL two necked flask equipped with reflux condenser and an inlet glass tube touching the bottom of the reaction flask. The inlet glass tube was connected to a 2 mL round-bottom flask, which contains 2.25 g (14.06 mmol) of bromine. Bromine vapors obtained by heating of the flask to 100 °C, were transferred directly to the refluxing solution (2–3 min) while stirring magnetically. The resulting reaction mixture was refluxed for 5 min. After being cooled to room temperature the solvent was evaporated. The oily residue was chromatographed on silica gel (110 g) eluting with hexane. The first fraction was the unreacted starting material **12** (1.0 g). From the other fractions four compounds were isolated in the following order: **13** (0.58 g, 37%), **15** (0.18 g, 12%), **14** (0.44 g, 17%), **16** (0.30 g, 11%). Then the column was eluted with ether/hexane (1:9) and 0.154 g (7%) of **17a** was isolated as the last fraction.

3.4.1. 2-(Bromomethyl)-1,2-dihydronaphthalene (13).[10] Pale yellow liquid (the second fraction), ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.21–7.04 (m, 4H, ArH), 6.55 (dd, J=9.7, 1.3 Hz, 1H, H_4), 5.93 (dd, J=9.7, 4.0 Hz, 1H, H_3), 3.44 (dd, J=9.9, 5.5 Hz, 1H, H_1), 3.33 (dd, J=9.9, 7.4 Hz, 1H, H_1), 2.95 (d, J=7.2 Hz, 2H, –CH_2Br), 2.87 (m, 1H, H_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.4, 135.1, 131.2, 131.1, 130.2, 129.6, 128.8, 128.2, 38.5, 38.1, 34.2.

3.4.2. 2-(Bromomethyl)naphthalene (15).[9,10] Colorless plates (the third fraction), mp 52–53 °C (lit.[9] 51–53 °C) from ethanol. ^{1}H NMR data for **15** were identical with those reported in the literature. ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.1, 135.2, 135.1, 130.7, 129.9, 129.8, 129.7, 128.7, 128.5, 128.4, 35.6.

3.4.3. 5,6,8-Tribromo-6,7,8,9-tetrahydro-5*H*-benzo[*a*]cycloheptene (14). Colorless plates (the fourth fraction), mp 105–106 °C from ether/hexane. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38–7.15 (m, 4H, ArH), 5.43 (d, J=5.2 Hz, 1H, H_5), 4.70 (m, 1H, H_6), 4.50 (tt, J=12.1, 2.1 Hz, 1H, H_8), 3.96 (dd, A-part of AB-system, J=14.3, 12.1 Hz, 1H, H_9), 3.54 (ddd, A-part of AB-system, J=14.9, 10.8, 3.0 Hz, 1H, H_7), 3.42 (dt, B-part of AB-system, J=14.3, 2.0 Hz, 1H, H_8), 2.90 (dm, B-part of AB-system, J=14.9 Hz, 1H, H_7); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 139.8, 138.3, 134.0 (−), 133.4 (−), 131.9 (−), 129.4 (−), 58.1 (−), 54.1 (−), 48.5, 47.6 (−), 47.3; ν_{max} (KBr) 3018, 2337, 1492, 1433, 1367, 1253, 1205, 1170, 1118, 1083, 931 cm^{-1}; MS (EI, *m*/*z*, % relative intensity) 386/384/382/380 (M^+, 0.6/2.2/2.3/0.6), 305/303/301 (M^+−Br, 12/22/11), 223.1/221.1 (M^+−2Br, 50/47), 142.2 (72), 141.1 (M^+−3Br, 100), 128.2 (76). Anal. Calcd for $C_{11}H_{11}Br_3$: C, 34.50; H, 2.90. Found: C, 34.85; H, 2.74.

3.4.4. 1,2-Dibromo-3-(bromomethyl)-1,2,3,4-tetrahydronaphthalene (16). Pale yellow powder (the fifth fraction), mp 72–74 °C from ether/hexane. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16 (dd, J=7.7 and 1.4 Hz, 1H, ArH), 7.07 (m, 2H, ArH), 6.93 (br d, J=7.3 Hz, 1H, ArH), 5.57 (d, J=2.2 Hz, 1H, H_1), 4.87 (br s, 1H, H_2), 3.33 (dd, A-part of AB-system, J=10.2, 5.9 Hz, 1H, –CH_2Br), 3.28 (dd, B-part of AB-system, J=10.2, 8.3 Hz, 1H, –CH_2Br), 2.87 (dd, A-part of AB-system, J=16.1, 5.1 Hz, 1H, H_4), 2.79 (m, 1H, H_3), 2.66 (dd, B-part of AB-system, J=16.1, 11.3 Hz, 1H, H_4); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.5 (s), 132.6 (s), 131. 1 (d), 129.1 (d), 129.0 (d), 127.1 (d), 55.3 (d), 51.3 (d), 36.01 (d), 35.1 (t), 30.6 (t); ν_{max} (KBr) 2845, 1490, 1425, 1336, 1234, 1143, 1097, 1031 cm^{-1}; MS (EI, *m*/*z*, % relative intensity) 386/384/382/380 (M^+, 0.5/1/0.8/0.4), 305/303/301 (M^+−Br, 11/23/13), 223/221 (M^+−2Br, 30/27), 143.1 (57), 141.1 (M^+−3Br, 100), 129.2 (97). Anal. Calcd for $C_{11}H_{11}Br_3$: C, 34.50; H, 2.90. Found: C, 34.38; H, 2.79.

3.4.5. 2-Bromo-3-(bromomethyl)-1,2,3,4-tetrahydronaphthalene-1-ol (17a). Colorless needles (the sixth fraction), mp 103–104 °C from ether/hexane. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55 (br d, J=6.8 Hz, 1H, ArH), 7.26 (m, 2H, ArH), 7.12 (br d, J=6.7 Hz, 1H, ArH), 4.95 (dd, J=9.1, 3.7 Hz, 1H, H_1), 4.18 (dd, J=11.1, 9.1 Hz, 1H, H_2), 3.79 (dd, A-part of AB-system, J=10.4, 5.3 Hz, 1H, –CH_2Br), 3.70 (dd, B-part of AB-system, J=10.4, 2.5 Hz, 1H, –CH_2Br), 3.02 (d, J=7.4 Hz, 2H, H_4), 2.80 (d, J=4.0 Hz, 1H, –OH), 2.44 (m, 1H, H_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.4 (s), 133.4 (s) 128.2 (d), 128.1 (d), 127.0 (d), 126.9 (d), 75.2 (d, C-1), 63.5 (d, C-2), 40.6 (t, –CH_2Br), 39.1 (d, C-3), 33.9 (t, C-4); ν_{max} (KBr) 3280, 2835, 1488, 1433, 1326, 1230, 1174, 1053, 1022, 904 cm^{-1}; MS (EI, *m*/*z*, % relative intensity) 322/320/318 (M^+, 9/18/11), 239/241 (M^+−Br, 95/100), 159 (M^+−2Br, 21). Anal. Calcd for $C_{11}H_{12}Br_2O$: C, 41.28; H, 3.78. Found: C, 41.01; H, 3.95.

3.5. Reaction of 1,2-dibromo-3-(bromomethyl)-1,2,3,4-tetrahydronaphthalene 16 with potassium *tert*-butoxide

To a stirred solution of tribromide **16** (100 mg, 0.26 mmol) in 5 mL of dry THF, potassium *tert*-butoxide (70 mg, 0.62 mmol) was added. The reaction mixture was heated at 60–70 °C for 3 h and then cooled to room temperature. The mixture was diluted with water (20 mL) and the aqueous solution was extracted with ether (3×30 mL), washed with water (20 mL), and dried over $CaCl_2$. Evaporation of the solvent gave an oil whose ^{1}H NMR spectrum indicated a mixture of **23** and **15** in a ratio of 84:16 (according to the ^{1}H NMR spectrum), respectively. The crude product was purified by preparative TLC (silica gel, hexane) to give 33 mg (57%) of **23** and 1.7 mg (3%) of **15**.

3.5.1. 1-Bromo-3-methylnaphthalene (23).[5c,13] Pale yellow liquid, ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.20 (m, 1H, ArH), 7.76–7.45 (m, 5H, ArH), 2.51 (s, 3H, –CH_3); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 138.4, 137.1, 134.3 (−), 132.7, 130.0 (−), 129.3 (2 ×,−), 129.1 (−), 128.7 (−), 125.0, 23.7 (−); ν_{max} (film) 3051, 2920, 2856, 1599, 1558, 1497, 1365, 1259, 1207, 854, 748 cm^{-1}.

3.6. Reaction of 2-(bromomethyl)-1,2-dihydronaphthalene 13 with potassium *tert*-butoxide

The reaction was carried out as described above by using 200 mg (0.83 mmol) of **13** and 150 mg (1.34 mmol) of potassium *tert*-butoxide. 2-Methylnaphthalene (83 mg, 65%) was obtained as a white solid.

3.7. Reduction of tribromide 14

Metallic sodium (116 mg, 5.04 mmol) was cut into small pieces and combined with 10 mL of anhydrous ether. This was magnetically stirred at reflux under nitrogen atmosphere while a mixture of tribromide **14** (127 mg, 0.33 mmol), *tert*-butanol (375 mg, 5.07 mmol), and ether (5 mL) was added dropwise over a period of 30 min. After stirring at reflux temperature for 48 h, the heat was removed and methanol (0.5 mL) and then water (1 mL) were added dropwise. The mixture was diluted with water (20 mL) and the aqueous solution was extracted with ether (3×50 mL), washed with water (20 mL), and dried over $CaCl_2$. After removal of the solvent, the residue was chromatographed on silica gel with hexane yielding 41 mg (85%) of **25**.[14]

3.7.1. 6,7,8,9-Tetrahydro-5*H*-benzo[*a*]cycloheptene (25).[14] Pale yellow oil, ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10 (s, 4H, ArH), 2.84 (m, 4H, benzylic protons), 1.88 (m, 2H), 1.71 (m, 4H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 144.4, 130.2 (−), 127.2 (−), 38.1, 34.1, 29.7; ν_{max} (film) 2922, 2854, 1454, 746 cm^{-1}.

3.8. Reaction of tribromide 14 with potassium *tert*-butoxide

The reaction was carried out as described for **16** by using 195 mg (0.51 mmol) of **14** and 125 mg (1.21 mmol) of potassium *tert*-butoxide. After workup, the residue was purified by TLC (silica gel, hexane) to give 8 mg (7%) of **23** and 50 mg (44%) of **24**.

3.8.1. 9-Bromo-5*H*-benzo[*a*]cycloheptene (24). Pale yellow oil, ^{1}H NMR (200 MHz, $CDCl_3$) δ (200 MHz, $CDCl_3$) 7.86 (dd, J=7.5, 1.8 Hz, 1H, ArH), 7.42–7.11 (m, 4H, H_8 and ArH), 5.99–5.84 (m, 2H, H_6 and H_7), 3.09 (d, J=5.8 Hz, 2H, H_5); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 139.7, 137.3, 133.2 (−), 131.5 (−), 130.8 (−), 130.3 (−), 128.3, 128.1 (−), 127.2 (−), 126.9 (−), 35.8; ν_{max} (film) 3028, 2924, 2850, 1585, 1439, 1169, 1043, 896, 760, 708 cm^{-1}; MS (EI, *m*/*z*, % relative intensity) 220/218 (M^+, 2), 139 (M^+−Br, 100), 115 (85), 86 (14). Anal. Calcd for $C_{11}H_9Br$: C, 59.76; H, 4.10. Found: C, 59.48; H, 4.21.

3.9. 2-Bromo-3-(bromomethyl)-1,2,3,4-tetrahydronaphthalen-1-yl acetate (17b)

To a stirred solution of alcohol **17a** (100 mg, 0.31 mmol) in 10 mL of CH_2Cl_2, acetyl chloride (0.245 g, 3.12 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. Evaporation of the solvent and excess acetyl chloride afforded a solid, which was then recrystallized from ether/hexane to give the dibromo acetate **17b** (92 mg, 81%) as white needles, mp 101–102 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32–7.12 (m, 4H, ArH), 6.34 (d, J=7.8 Hz, 1H, H_1), 4.36 (dd, J=9.7, 7.8 Hz, 1H, H_2), 3.83 (dd, A-part of AB-system, J=10.4, 5.3 Hz, 1H, –CH_2Br), 3.72 (dd, B-part of AB-system, J=10.4, 4.0 Hz, 1H, –CH_2Br), 3.21–2.99 (m, 2H, H_4), 2.54 (m, 1H, H_3), 2.22 (s, 3H, –CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.6, 136.1, 134.6, 130.6 (2×), 129.6, 129.0, 77.3, 56.5, 43.3, 40.2, 34.9, 23.1; ν_{max} (KBr) 3004, 2899, 2849, 1747, 1613, 1478, 1425, 1374, 1230, 1107, 1072, 1039, 915 cm^{-1}. Anal. Calcd for $C_{11}H_{12}Br_2O$: C, 41.28; H, 3.78. Found: C, 41.01; H, 3.95.

3.10. *exo*-Ethyl-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]-naphthalene-1-carboxylate (26)

The *exo*-ester **26** was prepared in 42% yield as described in the literature.[16] Comparison of the spectral data of this compound with those reported in the literature[4b] was in full agreement.

3.11. Bromination of *exo*-ester 26 at 77 °C

The reaction was carried out as described above by using 110 mg (0.51 mmol) of **26** and 170 mg (1.06 mmol) of bromine. After removal of the solvent, the residue was filtered through a short silica gel column and eluted with chloroform. Evaporation of the solvent afforded an oil, which was crystallized from ether/hexane to give the dibromo ester **27**[17] (118 mg, 62%).

3.11.1. *exo*-Ethyl-2,7-dibromo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene-1-carboxylate (27).[17] White solid, mp 123–124 °C, ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36–7.24 (m, 4H, ArH), 5.66 (t, J=1.4 Hz, 2H, benzylic), 4.12 (q, J=7.2 Hz, 2H, –OCH_2), 2.75 (dt, J=4.1, 1.4 Hz, 2H, cyclopropane), 1.46 (t, J=4.1 Hz, 1H, cyclopropane), 1.24 (t, J=7.2 Hz, –CH_3); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 172.1, 134.3, 132.3 (−), 131.9 (−), 63.1, 45.9 (−), 30.3 (−), 28.1 (−), 16.2 (−); ν_{max} (KBr) 2970, 2926, 1690, 1441, 1361, 1176, 1140, 1016, 913 cm^{-1}.

Acknowledgements

The authors are indebted to the Department of Chemistry (Faculty of Science and Faculty of Education) at Atatürk University and TUBITAK (MISAG-216) for financial support of this work and the State Planning Organization of Turkey (DPT) for purchasing a 200 MHz NMR and liquid nitrogen cryogenerator.

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