
Reactivity of the 5-hydroacenaphthylene anion towards electrophiles containing an additional functional group

5.1 Introduction

A useful tool in the synthesis of PAH is the reductive alkylation with electrophiles containing a second functional group. These compounds, such as an ester, a nitrile, a halide or a ketone, can be used in a second step for extension of the PAH skeleton, e.g. by cyclisation. Examples of this strategy are the syntheses of cyclopent[*hi*]aceanthrylene¹ and cyclopenta[*cd*]pyrene.² The sodium salt of bromoacetic acid was used as electrophile in the reaction of the anthracene dianion and the 5-hydropyrene anion. The resulting acids could easily be cyclised leading to an additional five-membered ring in an internal Friedel-Crafts acylation. Also, electrophiles with a nitrile or ester group can be used as precursors for ring closure reactions via acid chlorides. Methyl groups can now be introduced easily by using methylated electrophiles or by reaction of the resulting ketones with methyllithium.³

In the synthesis of benzo[*ghi*]perylene and coronene, bromoacetaldehyde diethyl acetal was reacted with the dianions of perylene and benzo[*ghi*]perylene to give expansion of the original PAH skeleton with 2 carbon atoms and, after ring closure, extension of the original structure with a six-membered ring.⁴

A third class of electrophiles which can be used for the expansion of PAHs via reductive alkylation are the dihaloalkanes. In a one-pot reaction the dihaloalkanes react twice with a PAH anion resulting in the addition of a (spiro-fused) ring to the anionic system.⁵ Reactions with the phenalene anion⁶ and the 5-hydropyrene anion⁷ gave high yields of cyclised products. In a subsequent step spiro-fused rings can be rearranged to ortho- or meta-fused rings, either photochemically or via a thermal reaction.⁶ The use of methyl-substituted dihaloalkanes leads directly to the methyl derivatives of the larger PAHs.⁸

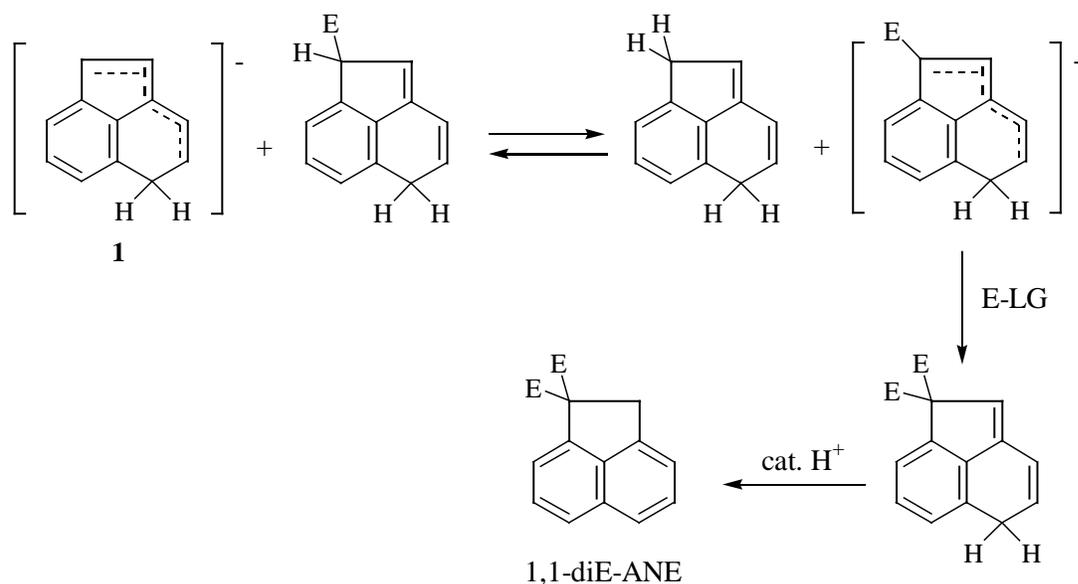
For the synthesis of PAHs containing heteroatoms such as sulfur and nitrogen, the direct formation of a carbon atom-heteroatom bond would open the way to novel PAHs.

In this chapter, reactions of the 5-hydroacenaphthylene anion are performed with a variety of electrophiles. In this manner substituents containing a functional group can be introduced or carbon-sulfur bonds can be created.

5.2 Results and discussion

The 5-hydroacenaphthylene anion **1** was prepared as described in Chapter 2. At -60°C one equivalent of electrophile was added (unless stated otherwise) and the reaction mixture was stirred for 15 minutes, after which the reaction was quenched with water. Extraction with diethyl ether, drying over magnesium sulfate and concentration *in vacuo* gave the substitution products.

The general reaction will predominantly give 1-substituted acenaphthenes, but in some cases also 1,1-disubstituted products are found (Scheme 1). In Table 1, the electrophiles that were used in the reactions with **1** are listed.



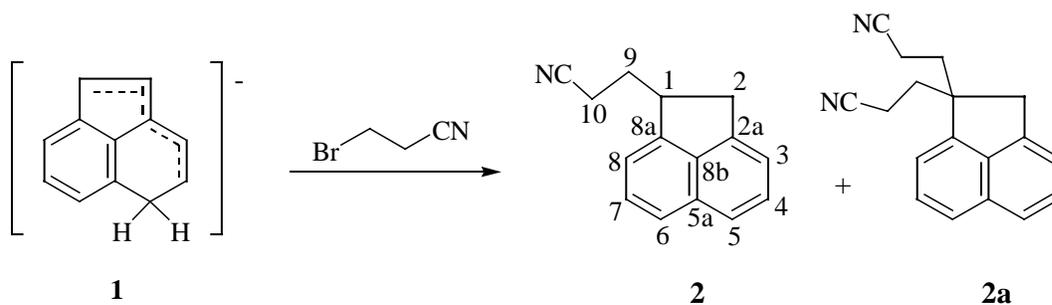
Scheme 1: Formation of disubstitution products in the reaction of **1** with electrophiles (E = electrophile, LG = leaving group, ANE = acenaphthene).

The products were characterised by NMR spectroscopy, infrared spectroscopy and GC-MS. In the NMR spectra the patterns of the acenaphthene moiety of the mono-substituted and 1,1-disubstituted acenaphthenes resemble those of 1-allyl- and 1,1-diallylacenaphthene (Chapter 3).

Table 1: Products of the reactions of **1** with electrophiles.

Electrophile	1-E-ANE	1,1-diE-ANE
3-Bromopropionitrile	2	2a
3-Iodopropionitrile	2	2a
Ethyl bromoacetate	3	
Ethyl iodoacetate	3	
Ethyl 3-bromopropanoate	4	
Ethyl 3-iodopropanoate	4	
Methyl thiocyanide	5	5a
Diphenyl disulfide		6a
1,4-Dibromobutane		7a
1,4-Diiodobutane		7a
1,5-Dibromopentane		8a
1,5-Diiodopentane		8a

In contrast to the reactions with methyl iodide, allyl bromide and benzyl bromide, the reactions of **1** with the more polar electrophiles gave lower yields of substitution products and also gave more side-products. In many reactions considerable amounts of acenaphthene were formed. One explanation is that the electrophiles are more hygroscopic than the alkyl halides and thus contain a larger amount of water. Therefore, the electrophiles should be carefully purified and dried before use to obtain the best results. The formation of side-products may be due to the presence and the reactivity of the second functional group.

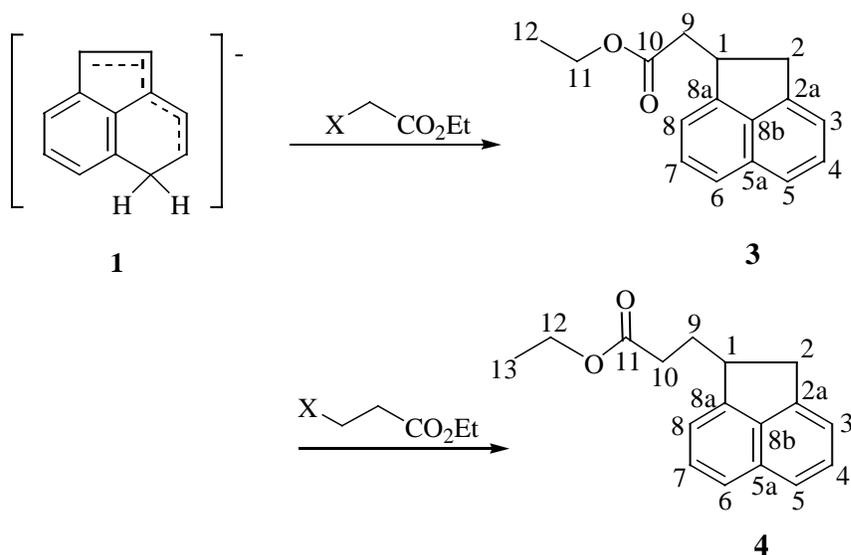
 ω -Halonitriles**Scheme 2:** Reaction of **1** with 3-bromopropionitrile.

The reaction of **1** with 3-bromopropionitrile gives mono- as well as disubstitution products in 20-60% and 5-50% yield, respectively (Scheme 2). The formation of disubstitution products can be explained by the reaction sequence shown in Scheme 1 (see also Chapter 3). The ratio of mono- and

di-substitution products depends strongly on the concentration of 3-bromopropionitrile: more electrophile leads to more disubstitution products. If only 1-(2-cyanoethyl)acenaphthene (**2**) is required, the reaction should be performed with only 0.5 equivalents of 3-bromopropionitrile. This product can easily be separated from acenaphthene by silica gel column chromatography. Next to the mono- and di-substitution products, traces of side-products containing olefinic protons are present. These could not be identified as 2a-substitution products (see Chapter 4) or as 1,5-dihydro-1-substituted acenaphthylenes. No further attempts were made to characterise these products.

The use of 3-iodopropionitrile instead of 3-bromopropionitrile leads to even more disubstitution product. This might be due to the fact that alkyl iodides react faster than alkyl bromides in S_N2 reactions.

Halo-esters



Scheme 3: Reaction of **1** with ethyl haloacetate and ethyl 3-halopropanoate ($X = Br, I$).

The reaction of **1** with ethyl bromoacetate (Scheme 3) gives ethyl acenaphthene-1-acetate **3** in relatively high yields (up to 90%). No di-substitution products were observed. The side-products with olefinic protons were not stable towards exposure to air. They might include the initial 1-substituted 1,5-dihydroacenaphthylene. The use of ethyl iodoacetate gave the same substitution pattern, but yielded more acenaphthene, which is probably caused by traces of water in the ethyl iodoacetate.

Ethyl acenaphthene-1-acetate (**3**) can easily be hydrolysed into the corresponding acid quantitatively. The synthesis of this acid was reported before, starting from 1-acenaphthenol.⁹ In three steps the alcohol was converted via the bromide and the malonic acid derivative to the acid in

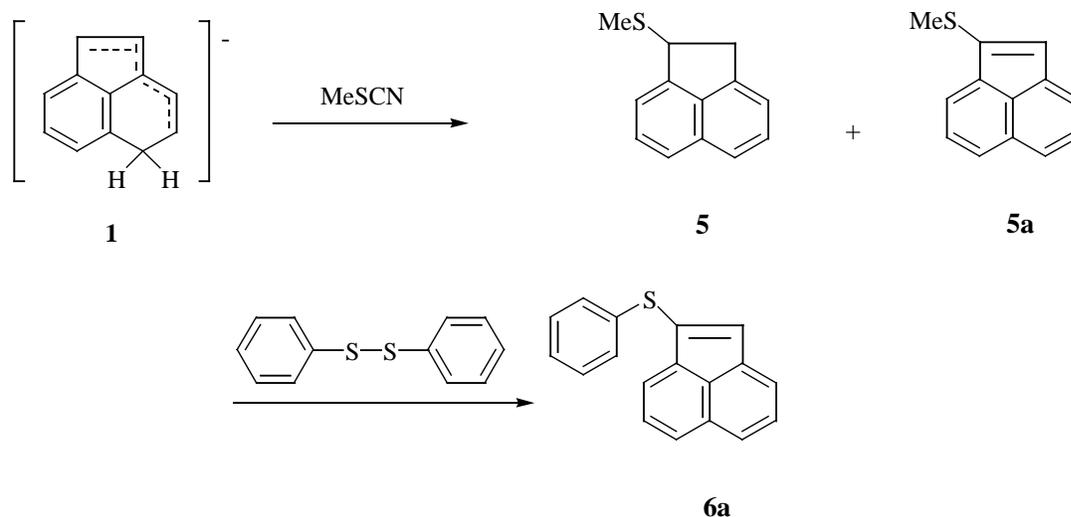
70% yield. 1-Acenaphthenol, however, is rather expensive (25 g, ca. NLG 200) compared to acenaphthylene (100 g, ca. NLG 70,00). Therefore, our shorter route is preferable to the synthesis reported earlier.

Ethyl acenaphthene-1-propanoate (**4**) is the major product from the reaction of **1** with ethyl 3-bromopropanoate and could be isolated in 30-60% yield. Again, side-products containing olefinic protons are observed. The yield of the reaction is considerably lower than in the case of the reaction of ethyl bromoacetate. A possible explanation is that the side-chain of **4** is deprotonated by **1**. The side products could not be characterised. Remarkable is the presence of traces of carboxylic acids in the product mixture.

The yield of ethyl acenaphthene-1-propanoate (**4**) could be elevated by changing from ethyl 3-bromo- to ethyl 3-iodopropanoate. Now, less side-products and more **4** were isolated. Conversion from the ester into the acid could be accomplished by dissolving the ester in ethanol and boiling under reflux for several hours with KOH. Certainly, this synthesis is much more convenient than the synthesis from acenaphthene-1-acetic acid as proposed by Bachmann and Sheehan.⁹ Acenaphthene-1-propanoic acid can be cyclised via a Friedel-Crafts acylation and converted into cyclopenta[*def*]phenanthrene.⁹

Bromoacetaldehyde diethylacetal is expected to react via the SET mechanism^{10,11} with **1** and thus products with substituents at position 2a should be found. However, reaction of **1** with bromoacetaldehyde diethylacetal gave only low yields of substitution products which were not further isolated and characterised.

Sulfur electrophiles

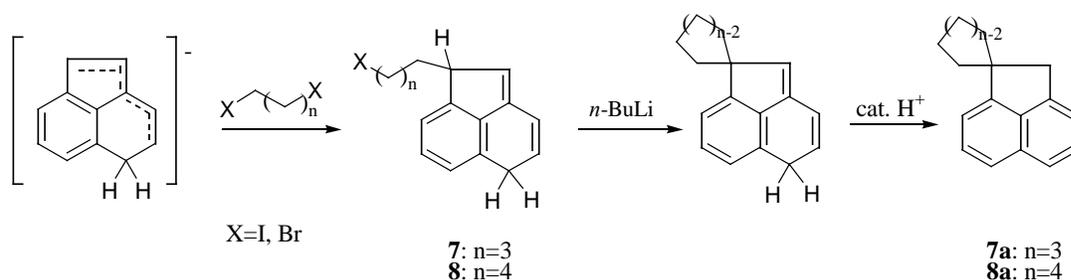


Scheme 4: Reaction of **1** with methyl thiocyanate and diphenyl disulfide.

Reaction of **1** with methyl thiocyanide gave 1-(methylthio)acenaphthene (**5**) and 1-(methylthio)acenaphthylene (**5a**) in equal amounts (both in 25% yield) (Scheme 4). Oxidation of 1-(methylthio)acenaphthene (**5**) to 1-(methylthio)acenaphthylene (**5a**) is not likely to occur, because **5** could be isolated by silica gel column chromatography and was stable towards exposure to air for several weeks without conversion into **5a**. Therefore, elimination of methanethiol from the 1,1-bis(methylthio)acenaphthene seems the most reasonable explanation for the formation of **5a**. Variation in the amount of methyl thiocyanide added to the reaction mixture would give conditions for the more selective synthesis of one of the two products.

A similar reaction was performed using diphenyl disulfide as electrophile. One major reaction product was obtained: 1-(phenylthio)acenaphthylene **6a** in 43% yield (Scheme 4). The formation of **6a** can again be explained by the elimination of thiophenol from 1,1-bis(phenylthio)acenaphthene. It can also be concluded that under these conditions no monosubstituted acenaphthene is formed. Probably the acidity of 1-(phenylthio)-1,5-dihydroacenaphthylene is higher than that of 1,5-dihydroacenaphthylene, resulting in the formation of the substituted hydroanion in high yields. If 1-(phenylthio)acenaphthene is desired, the reaction of **1** should be performed with a lower concentration of diphenyl disulfide.

α,ω -Dihaloalkanes



Scheme 5: Reaction of **1** with dihaloalkanes.

The reaction of **1** with 1,4-dihalobutane and 1,5-dihalopentane gave predominantly substitution at position 1. When 1,1-disubstitution occurred, the internal reaction was always favoured over reaction with a second dihaloalkane: no 1,1-di(haloalkane)-acenaphthenes were isolated. The yield of the so-formed spiro-fused rings could be elevated by the addition of *n*-butyllithium to the reaction mixture (Scheme 5).

Following this procedure spiro[acenaphthene-1,1'-cyclopentane] **7a** and spiro[acenaphthene-1,1'-cyclohexane] **8a** could be isolated in 35% and 40% yield, respectively. Because of the difficult silica gel chromatography separation of monosubstitution products and cyclised products, the former were not isolated, but directly used in the reaction with *n*-butyllithium. The reactions with

diiodoalkanes, especially with 1,2-diiodoethane and 1,3-diiodopropane, gave small amounts of 2a-substituted products. In these reactions the SET mechanism plays a more important role (see Chapter 4). The products were identified by NMR spectroscopy but no attempts for further isolation and characterisation were performed. It was remarkable that no cyclisation products of the reactions with 1,2-dihaloethane were observed.

5.3 Conclusions

The reaction of the 5-hydroacenaphthylene anion with electrophiles containing a second functional group proceeds at position 1 and provides an easy and fast route to 1-substituted acenaphthenes. These new 1-substituted acenaphthenes can be used for the synthesis of higher derivatives of acenaphthene. 3-Bromopropionitrile, 1,4-dibromobutane and 1,5-dibromopentane, and their iodo-analogues, give rise to 1,1-disubstitution products, in the case of the dihaloalkanes resulting in spiro-fused rings. In the reaction of **1** with diphenyl disulfide and methyl thiocyanide a carbon-sulphur bond is created. In these reactions the disubstituted products undergo an elimination reaction resulting in 1-substituted acenaphthylenes.

5.4 Experimental section

General: Acenaphthylene (Aldrich, 75%) was purified by treatment with DDQ and filtration over silica. The electrophiles were obtained from Acros, Aldrich and Merck and used without further purification but dried over molecular sieves (3A, 8-12 mesh). 3-Iodopropionitrile, ethyl iodoacetate and ethyl 3-iodopropanoate were prepared from the corresponding bromides by bromine-iodine exchange with potassium iodide in acetone. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^1H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. All chemical shift data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (J) are given in Hz. Identification of the products was performed using ^1H - ^1H and ^1H - ^{13}C correlated 2D NMR spectra. For the determination of the coupling constants we used the simulation program PERCH.¹²

General procedure:

Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. Acenaphthylene (0.76 g, 5 mmol) was added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during

which the temperature was kept at 0°C, a deep green solution was obtained. The flask was then cooled in an ethanol-nitrogen bath to -70°C and methanol (0.146 ml, 5 mmol) was added. The colour of the mixture turned red. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. The mixture was cooled again to -70°C and 5 mmol of electrophile were added. Stirring was continued at room temperature for 30 minutes after which period the reaction was quenched with water. The addition of light petroleum (boiling range 40-60°C), extraction with water, washing with brine, drying over MgSO₄ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. Yields of substitution products are variable, generally between 30 and 90%, depending on the humidity of the air in the laboratory and the reactivity of the electrophile. The composition of the mixture was determined by means of NMR spectroscopy.

Reaction of 1 with 3-bromopropionitrile:

To a solution of **1** (5 mmol) 3-bromopropionitrile (0.45 ml, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded two products: 1-(2-cyanoethyl)acenaphthene (20-60%) and 1,1-bis(2-cyanoethyl)acenaphthene (5-50%).

1-(2-Cyanoethyl)acenaphthene (2)

¹H NMR (CDCl₃, TMS) δ: 7.63 (ddd, $J_{6,7} = 8.2$, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.60 (dddd, $J_{4,5} = 8.1$, $J_{2,5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.46 (dd, $J_{6,7} = 8.2$, $J_{7,8} = 7.1$, 1 H, H-7), 7.45 (dd, $J_{4,5} = 8.1$, $J_{3,4} = 7.1$, H-4), 7.26 (d, $J_{3,4} = 7.1$, $J_{2,3}$, $J_{2',3}$, 1 H, H-3), 7.24 (ddd, $J_{7,8} = 7.1$, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 3.79 (dddddd, $J_{1,2} = 8.2$, $J_{1,2'} = 4.2$, $J_{1,9} = 4.5$, $J_{1,9'} = 8.7$, $J_{1,6}$, $J_{1,8}$, 1 H, H-1), 3.60 (dddd, $J_{1,2} = 8.2$, $J_{2,2'} = -17.5$, $J_{2,3}$, $J_{2,5}$, 1 H, H-2), 3.00 (dddd, $J_{1,2'} = 4.2$, $J_{2,2'} = -17.5$, $J_{2,3}$, $J_{2',5}$, 1 H, H-2'), 2.40 (dd, $J_{9,10} = 7.3$, $J_{9',10} = 7.2$, 2 H, H-10), 2.20 (ddt, $J_{9,9'} = -14.4$, $J_{1,9} = 4.5$, $J_{9,10} = 7.3$, 1 H, H-9), 1.97 (ddt, $J_{9,9'} = -14.4$, $J_{1,9'} = 8.7$, $J_{9',10} = 7.2$, 1 H, H-9'), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

¹³C NMR (CDCl₃) δ: 146.7 (C-2a or C-8a), 143.2 (C-2a or C-8a), 138.3 (C-8b), 131.4 (C-5a), 128.0 (C-7), 127.7 (C-4), 123.3 (C-6), 122.5 (C-5), 119.5 (CN), 119.5 (C-3), 118.9 (C-8), 42.0 (C-1), 36.7 (C-2), 31.6 (C-9), 14.9 (C-10).

1,1-Bis(2-cyanoethyl)acenaphthene (2a)

¹H NMR (CDCl₃, TMS) δ: 7.72 (ddd, $J_{6,7} = 8.9$, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.67 (dddd, $J_{4,5} = 8.8$, $J_{2,5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.54 (dd, $J_{6,7} = 8.9$, $J_{7,8} = 6.9$, 1 H, H-7), 7.51 (dd, $J_{4,5} = 8.8$, $J_{3,4} = 6.9$, H-4), 7.31 (dddd, $J_{3,4} = 6.9$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$, 1 H, H-3), 7.19 (ddd, $J_{7,8} = 6.9$, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 3.30 (s, 2 H, H-2), 2.21 (dd, $J_{9,10} = 8.5$, $J_{9',10} = 7.8$, 4 H, H-10), 2.06 (dt, $J_{9,9'} = -16.2$, $J_{9,10} = 8.5$, 2 H, H-9), 1.86 (dt, $J_{9,9'} = -16.2$, $J_{9',10} = 7.8$, 2 H, H-9'), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

¹³C NMR (CDCl₃) δ: 145.3 (C-2a or C-8a), 140.8 (C-2a or C-8a), 138.2 (C-8b), 131.4 (C-5a), 128.6 (C-4 or C-7), 128.1 (C-4 or C-7), 124.6 (C-5 or C-6), 123.2 (C-5 or C-6), 120.0 (C-3 or C-8), 119.3 (CN), 118.3 (C-3 or C-8), 50.1 (C-1), 40.6 (C-2), 36.7 (2 C-10), 12.7 (2 C-9).

IR (pure liquid) cm^{-1} : 3040, 2970, 2920, 2860, 2240, 1600, 1480, 1460, 1420, 1380, 1350, 1290, 1120, 915, 810, 780, 730, 645.

MS m/z (%): 54 (8), 75 (3), 87 (2), 100 (1), 115 (1), 165 (100), 178 (3), 206 (28), 219 (1), 260 (15).

Reaction of 1 with ethyl bromoacetate:

To a solution of **1** (5 mmol) ethyl bromoacetate (0.554 ml, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded ethyl acenaphthene-1-acetate (40-90%).

Ethyl acenaphthene-1-acetate (3)

^1H NMR (CDCl_3 , TMS) δ : 7.56 (dddd, $J_{4,5} = 8.1$, $J_{2,5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.54 (ddd, $J_{6,7} = 8.1$, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.39 (dd, $J_{6,7} = 8.1$, $J_{7,8} = 7.4$, 1 H, H-7), 7.38 (dd, $J_{4,5} = 8.1$, $J_{3,4} = 7.4$, 1 H, H-4), 7.19 (dddd, $J_{3,4} = 7.4$, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1 H, H-3), 7.19 (ddd, $J_{7,8} = 7.4$, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 4.15 (q, $J_{11,12} = 7.1$, 2 H, H-11), 4.05 (dddddd, $J_{1,2} = 8.1$, $J_{1,2'} = 3.6$, $J_{1,9} = 5.6$, $J_{1,9'} = 9.4$, $J_{1,6}$, $J_{1,8}$, 1 H, H-1), 3.63 (dddd, $J_{1,2} = 8.1$, $J_{2,2'} = -17.5$, $J_{2,3}$, $J_{2,5}$, 1 H, H-2), 3.02 (dddd, $J_{2,2'} = -17.5$, $J_{1,2'} = 3.6$, $J_{2',3}$, $J_{2',5}$, 1 H, H-2'), 2.80 (dd, $J_{9,9'} = -15.8$, $J_{1,9} = 5.6$, 1 H, H-9), 2.52 (dd, $J_{9,9'} = -15.8$, $J_{1,9'} = 9.4$, 1 H, H-9'), 1.21 (t, $J_{11,12} = 7.1$, 3 H, H-12), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR (CDCl_3) δ : 172.2 (C-10), 147.4 (C-2a or C-8a), 143.7 (C-2a or C-8a), 138.1 (C-8b), 131.3 (C-5a), 127.8 (C-4 or C-7), 127.6 (C-4 or C-7), 122.9 (C-5 or C-6), 122.2 (C-5 or C-6), 119.2 (C-3 or C-8), 118.6 (C-3 or C-8), 60.3 (C-11), 40.7 (C-9), 39.3 (C-1), 37.7 (C-2), 14.1 (C-12).

IR (pure liquid) cm^{-1} : 2840, 1710, 1665, 1600, 1490, 1460, 1425, 1355, 1270, 1230, 1020.

GC-MS $m/z = 240$ is major product.

Reaction of 1 with ethyl bromopropanoate:

To a solution of **1** (5 mmol) ethyl 3-bromopropanoate (0.650 ml, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded Ethyl acenaphthene-1-propanoate (30-60%).

Ethyl acenaphthene-1-propanoate (4)

^1H NMR (CDCl_3 , TMS) δ : 7.57 (ddd, $J_{6,7} = 8.2$, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.55 (dddd, $J_{4,5} = 8.2$, $J_{3,5}$, $J_{2,5}$, $J_{2',5}$, 1 H, H-5), 7.41 (dd, $J_{6,7} = 8.2$, $J_{7,8} = 7.0$, 1 H, H-7), 7.40 (dd, $J_{4,5} = 8.2$, $J_{3,4} = 6.9$, H-4), 7.24 (ddd, $J_{7,8} = 7.0$, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.20 (dddd, $J_{3,4} = 6.9$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$, 1 H, H-3), 4.10 (q, $J_{12,13} = 7.2$, 2 H, H-12), 3.64 (dddddd, $J_{1,2} = 8.3$, $J_{1,2'} = 3.6$, $J_{1,9} = 5.0$, $J_{1,9'} = 6.1$, $J_{1,6}$, $J_{1,8}$, 1 H, H-1), 3.50 (dddd, $J_{2,2'} = -17.2$, $J_{1,2} = 8.3$, $J_{2,3}$, $J_{2,5}$, 1 H, H-2), 2.97 (dddd, $J_{2,2'} = -17.2$, $J_{1,2'} = 3.6$, $J_{2',3}$, $J_{2',5}$, 1 H, H-2'), 2.38 (dd, $J_{9,10} = 6.6$, $J_{9',10} = 7.1$, 2 H, H-10), 2.20 (ddt, $J_{9,9'} = -15.3$, $J_{1,9} = 5.0$, $J_{9,10} = 6.6$, 1 H, H-9), 1.94 (ddt, $J_{9,9'} = -15.3$, $J_{1,9'} = 6.1$, $J_{9',10} = 7.1$, 1 H, H-9'), 1.20 (t, $J_{12,13} = 7.2$, 3 H, H-13), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{2',3}$, $J_{2',5}$, $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR (CDCl_3) δ : 173.3 (C-11), 148.1 (C-2a or C-8a), 143.9 (C-2a or C-8a), 138.4 (C-8b), 131.3 (C-5a), 127.7 (C-4 or C-7), 127.6 (C-4 or C-7), 122.7 (C-5 or C-6), 122.2 (C-5 or C-6), 119.7 (C-3 or C-8), 119.1 (C-3 or C-8), 60.2 (C-12), 42.4 (C-1), 35.2 (C-2), 31.8 (C-9), 31.1 (C-10), 14.1 (C-13).

IR (pure liquid) cm^{-1} : 3040, 2980, 2940, 2920, 1730, 1600, 1495, 1440, 1370, 1300, 1255, 1175, 1030, 800, 770.

MS m/z (%): 42 (8), 63 (4), 89 (2), 115 (2), 167 (100), 209 (12), 225 (1), 254 (90).

Reaction of 1 with methyl thiocyanide:

To a solution of **1** (5 mmol) methyl thiocyanide (0.34 ml, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded two products: 1-(methylthio)acenaphthene (25%) and 1-(methylthio)acenaphthylene (25%).

1-(Methylthio)acenaphthene (5)

^1H NMR (200 MHz, CDCl_3 , TMS) δ : 7.68 (d, $J_{4,5} = 8.2$, 1 H, H-5), 7.63 (d, $J_{6,7} = 8.2$, 1 H, H-6), 7.48 (dd, $J_{6,7} = 8.2$, $J_{7,8} = 6.7$, 1 H, H-7), 7.44 (dd, $J_{4,5} = 8.2$, $J_{3,4} = 6.7$, 1 H, H-4), 7.37 (d, $J_{3,4} = 6.7$, 1 H, H-3), 7.24 (d, $J_{7,8} = 6.7$, 1 H, H-8), 3.88-3.77 (m, 3 H, H-1 and H-2), 2.12 (s, 3 H, -SMe).

^{13}C NMR (CDCl_3) δ : 140.3 (C-2a and C-8a), 136.1 (C-8b), 131.5 (C-5a), 128.1 (C-4 or C-7), 127.9 (C-4 or C-7), 124.7 (C-5 or C-6), 123.0 (C-5 or C-6), 119.4 (C-3 or C-8), 119.2 (C-3 or C-8), 63.0 (C-1), 49.2 (C-2), 15.8 (-SMe).

1-(Methylthio)acenaphthylene (5a)

^1H NMR (200 MHz, CDCl_3 , TMS) δ : 7.78 (d, $J_{4,5} = 8.2$, 1 H, H-5), 7.68 (d, $J_{6,7} = 5.5$, 1 H, H-6), 7.62 (dd, $J_{6,7} = 5.5$, $J_{7,8} = 3.9$, 1 H, H-7), 7.51 (dd, $J_{4,5} = 8.2$, $J_{3,4} = 6.9$, 1 H, H-4), 7.43 (d, $J_{3,4} = 6.9$, 1 H, H-3), 7.42 (d, $J_{7,8} = 3.9$, 1 H, H-8), 6.56 (s, 1 H, H-2), 2.60 (s, 3 H, -SMe).

Reaction of 1 with diphenyl disulfide:

To a solution of **1** (5 mmol) diphenyl disulfide (1.09 g, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes. After normal work-up, purification by silica gel column chromatography yielded 1-(phenylthio)acenaphthylene (43%).

1-(Phenylthio)acenaphthylene (6a)

^1H NMR (CDCl_3 , TMS) δ : 7.70 (d, $J_{4,5} = 8.1$, 1 H, H-5), 7.65 (d, $J_{6,7} = 7.8$, $J_{6,8} = 1.1$, 1 H, H-6), 7.52-7.35 (m, 6 H, H-4, H-7, H-3, H-8, and H-o or H-m), 7.25-7.17 (m, 3 H, H-p and H-o or H-m), 6.90 (s, 1 H, H-2).

^{13}C NMR (CDCl_3) δ : 138.4 (C-2a and C-8a), 135.8 (C-8b), 134.9 (C-5a), 130.5 (C-o or C-m), 129.7 (C-2), 129.0 (C-o or C-m), 127.9 (C-1 and C-i), 127.8 (C-4 or C-7), 127.7 (C-5), 127.5 (C-4 or C-7), 126.9 (C-p), 126.8 (C-6), 123.1 (C-3 or C-8), 123.0 (C-3 or C-8).

Reaction of 1 with 1,4-dibromobutane:

To a solution of **1** (5 mmol) 1,4-dibromobutane (0.60 ml, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes at room temperature. The solution was cooled again to -60°C and *n*-butyllithium (3.1 ml, 1.6 M in hexane, 5 mmol) was added. The reaction mixture was stirred for a

further 30 minutes and then quenched with water. After normal work-up, purification by silica gel column chromatography yielded spiro[acenaphthene-1,1'-cyclopentane] (35%).

Spiro[acenaphthene-1,1'-cyclopentane] (7a)

¹H NMR (CDCl₃, TMS) δ: 7.55 (dd, $J_{6,7} = 8.2$, $J_{6,8}$, 1 H, H-6), 7.52 (dddd, $J_{4,5} = 8.2$, $J_{3,5}$, $J_{2,5}$, 1 H, H-5), 7.41 (dd, $J_{6,7} = 8.2$, $J_{7,8} = 6.9$, 1 H, H-7), 7.38 (dd, $J_{4,5} = 8.2$, $J_{3,4} = 6.7$, H-4), 7.19 (dddd, $J_{3,4} = 6.7$, $J_{3,5}$, $J_{2,3}$, 1 H, H-3), 7.12 (dd, $J_{7,8} = 6.9$, $J_{6,8}$, 1 H, H-8), 3.16 (dd, $J_{2,3}$, $J_{2,5}$, 2 H, H-2), 1.90-1.79 (m, 8 H, H-cyclopentyl), $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{3,5}$ were observed but could not exactly be determined.

Reaction of 1 with 1,5-dibromopentane:

To a solution of **1** (5 mmol) 1,5-dibromopentane (0.68 ml, 5 mmol) was added at -60°C and the solution was stirred for 30 minutes at room temperature. The solution was cooled again to -60°C and *n*-butyllithium (3.1 ml, 1.6 M in hexane, 5 mmol) was added. The reaction mixture was stirred for a further 30 minutes and then quenched with water. After normal work-up, purification by silica gel column chromatography yielded spiro[acenaphthene-1,1'-cyclohexane] (40%).

Spiro[acenaphthene-1,1'-cyclohexane] (8a)

¹H NMR (CDCl₃, TMS) δ: 7.61 (dd, $J_{6,7} = 8.2$, $J_{6,8}$, 1 H, H-6), 7.61 (dddd, $J_{4,5} = 8.2$, $J_{3,5}$, $J_{2,5}$, 1 H, H-5), 7.48 (dd, $J_{6,7} = 8.2$, $J_{7,8} = 6.9$, 1 H, H-7), 7.46 (dd, $J_{4,5} = 8.2$, $J_{3,4} = 6.7$, H-4), 7.27 (dddd, $J_{3,4} = 6.7$, $J_{3,5}$, $J_{2,3}$, 1 H, H-3), 7.22 (dd, $J_{7,8} = 6.9$, $J_{6,8}$, 1 H, H-8), 3.28 (dd, $J_{2,3}$, $J_{2,5}$, 2 H, H-2), 1.80 (m, 4 H, H-10 and H-12), 1.71 (m, 2 H, H-11), 1.57 (m, 4 H, H-9 and H-13), $J_{6,8}$, $J_{2,3}$, $J_{2,5}$, $J_{3,5}$ were observed but could not exactly be determined.

¹³C NMR (CDCl₃) δ: 148.1 (C-2a or C-8a), 143.9 (C-2a or C-8a), 138.4 (C-8b), 131.3 (C-5a), 127.9 (C-4 or C-7), 127.8 (C-4 or C-7), 122.6 (C-5 or C-6), 122.2 (C-5 or C-6), 119.2 (C-3 or C-8), 117.5 (C-3 or C-8), 48.5 (C-1), 42.5 (C-2), 38.7 (C-10 and C-12), 25.8 (C-11), 23.5 (C-9 and C-13).

IR (pure liquid) cm⁻¹: 3040, 1730, 1480, 1030, 800, 770, 730.

MS m/z (%): 42 (8), 63 (4), 89 (2), 115 (2), 167 (100), 209 (12), 225 (1), 254 (90).

5.5 References

- 1 B.B. Boere, P.P.J. Mulder, J. Cornelisse, J. Lugtenburg *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 463-466
- 2 C. Tintel, J. Cornelisse, J. Lugtenburg *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 14
- 3 E.R. Kellenbach, J. Lugtenburg, J. Cornelisse *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 437-440
- 4 J.T.M. van Dijk, A. Hartwijk, A.C. Bleeker, J. Lugtenburg, J. Cornelisse *J. Org. Chem.* **1996**, *61*, 1136-1139
- 5 J.T.M. van Dijk, B.J. van de Panne, A.C. Bleeker, J. Lugtenburg, J. Cornelisse *Tetrahedron* **1996**, *52*, 2647-2662
- 6 M.A. Hempenius, J. Lugtenburg, J. Cornelisse *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 403-409
- 7 J.T.M. van Dijk, J. Lugtenburg, J. Cornelisse *J. Chem. Soc., Perkin Trans. 2* **1995**, 1489-1495
- 8 M.A. Hempenius, J. Lugtenburg, J. Cornelisse *J. Chem. Soc., Perkin Trans. 1* **1991**, 635-638
- 9 W.E. Bachmann, J.C. Sheehan *J. Am. Chem. Soc.* **1941**, *63*, 204-205
- 10 G.M. Stork *J. Am. Chem. Soc.* **1973**, *95*, 2014
- 11 M. Kuhn *J. Prakt. Chem.* **1940**, *156*, 103
- 12 R. Laatikainen, M. Niemitz, U. Weber, J. Sundelin, T. Hassinen, J. Vepsaelaeinen *J. Magn. Reson.* **1996**, *120*, 1-10