6

Reactions of the acenaphthylene dianion

6.1 Introduction

The acenaphthylene dianion **1** reacts with protons and methyl iodide selectively at position 5 (Chapter 2). The latter reaction is supposed to proceed via an S_N2 mechanism. However, in Chapter 4 we have seen that the 5-hydroacenaphthylene anion **2** can react via S_N2 as well as via single electron transfer (SET). The reaction path depends on the ability of the electrophile to accept an electron. A lower reduction potential and more steric bulk of the electrophile contribute to more SET character of the reaction. Because the electron-donating capacity of **1** is even higher than that of **2**, the probability of the occurrence of the SET mechanism is expected to be higher. In this chapter we study the reaction of **1** with a variety of electrophiles in order to elucidate the mechanism of the reductive alkylation of acenaphthylene.

6.2 Results

The acenaphthylene dianion (**1**) was prepared starting from acenaphthylene using 2.2 equivalents of sodium in anhydrous THF and ultrasonic vibration (see Chapter 2).

At -70 ºC one equivalent of electrophile was added to the reaction mixture and the solution was stirred at room temperature for 30-60 minutes. After cooling to -70 ºC the reaction was quenched with water. Addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. These oils were analysed by means of GC-MS and NMR techniques.

Most electrophiles gave complex mixtures of products upon reaction with **1**. In several cases these mixtures could not be separated into their components and the products could thus not be identified and characterised. When (bromomethyl)cyclopropane and allyl bromide were used, product isolation and identification turned out to be possible and conclusions about the reactivity of the dianion could be drawn. In other cases, the NMR and GC-MS data of the crude products mixtures provided indications about the interaction between the acenaphthylene dianion and the electrophile.

When one equivalent of (bromomethyl)cyclopropane was added to the acenaphthylene dianion (**1**), 5-(cyclopropylmethyl)acenaphthene was the major product (>90%) that could be isolated.

Addition of one equivalent of allyl bromide to the dianion **1** led, after work-up, to the isolation of a mixture of substitution products. This mixture could be separated with preparative gas chromatography. The major substitution products were identified by means of NMR as 1-allylacenaphthene (**3a**) (39% of substitution products), 5-allylacenaphthene (**3b**) (21%), 1,2-diallylacenaphthene (**3c**, one isomer, probably trans) (17%) and 1,5-diallylacenaphthene (**3d**) (12%). Next to these products probably 1-allylacenaphthylene (**3e**) (5%) and a third diallylacenaphthene (**3f**) (6%) were present. Because only one equivalent of allyl bromide was added, acenaphthene and acenaphthylene were also formed.

Reaction of **1** with 3,3-dimethylallyl bromide also gave a complex mixture of products. Comparison of the ^{1}H NMR spectrum with those of compounds **3** learned that the methyl groups were present at the olefinic as well as the allylic position.

Reaction of **1** with electrophiles containing a second functional group − in particular bromoacetonitrile, acetyl chloride, benzyl chloride, ethyl bromoacetate, diphenyl disulfide and methyl thiocyanide − gave acenaphthylene as the major product. Traces of substitution products were detected using GC-MS.

Reaction of bromoacetaldehyde diethylacetal with **1** gave a complex mixture of mono- and disubstitution products. The substitution pattern was similar to that in the reaction of **1** with allyl bromide. Next to the expected 5-substituted acenaphthene also 1-, 1,2-di- and 1,5-disubstitution products were observed. The monosubstitution products could be separated from the disubstitution products with silica gel column chromatography. However, the isolation of the individual isomers was not possible in this way. Therefore, no exact characterisation could be made for the isomers.

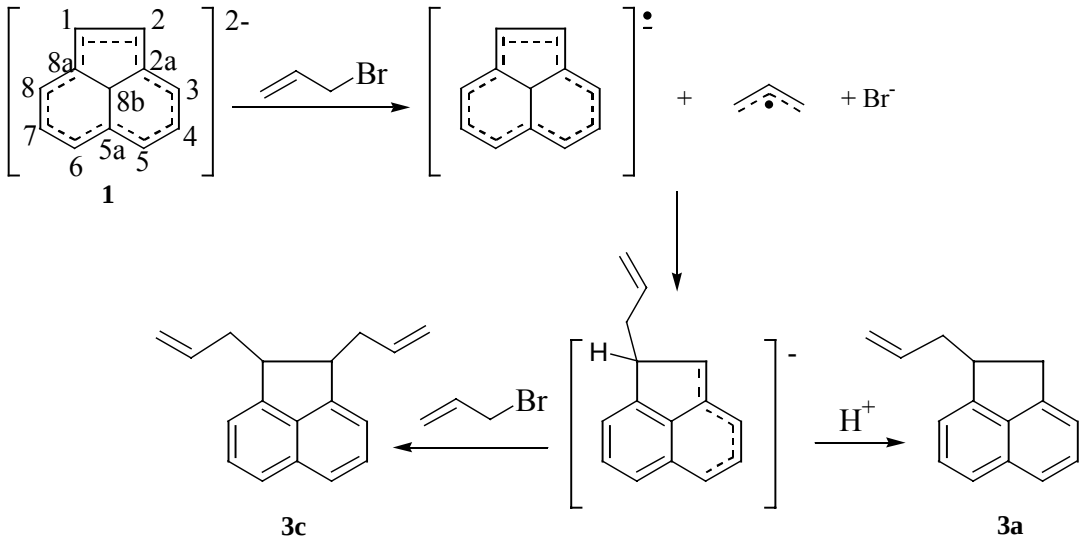
Reaction of **1** with one equivalent of bromobenzene resulted in a mixture of substitution products. GC-MS analysis showed three monophenylacenaphthenes and two monophenylacenaphthylenes. Next to these products a bromo-phenylacenaphthene was observed. The product mixture could not be separated by silica gel column chromatography, HPLC or preparative gas chromatography. Because of the presence of so many isomers and the complexity of the NMR spectrum (all peaks in the aromatic region), the products could not be identified with NMR spectroscopy.

The same reaction was performed with *p*-bromotoluene as electrophile. GC-MS analyses showed that this reaction also gave three mono(methylphenyl)acenaphthenes and one bromine containing derivative. In this case no acenaphthylene derivatives were observed. Remarkable was the presence of dimethylbiphenyl.

In the reaction of **1** with E/Z β-bromostyrene GC-MS showed the presence of one major substitution product (monosubstituted) and two side products (one mono- and one disubstitution product).

6.3 Discussion

The reaction of the acenaphthylene dianion with simple alkyl halides takes place selectively at position 5. The mechanism of this reaction is expected to be S_N2. However, single electron transfer (SET) may also play a role in the mechanism because of the high reactivity of the acenaphthylene dianion. To obtain evidence for the occurrence of SET in the reaction of **1** with simple alkyl halides, (bromomethyl)cyclopropane was used. If SET would be part of the mechanism, butene-substituted acenaphthenes should be present in the reaction mixture (see Chapter 3). Because no such products were found it may be concluded that (bromomethyl)cyclopropane and probably also other alkyl bromides, react with the acenaphthylene dianion via the S_N2 mechanism. Next to 5-(cyclopropylmethyl)acenaphthene, small amounts of acenaphthene and 5-(cyclopropylmethyl)-acenaphthylene were detected with GC-MS (<5%).



***Scheme 1**: Reaction of **1** with allyl bromide via SET.*

Allyl bromide reacts with the 5-hydroacenaphthylene anion (**2**) via S_N2 (Chapter 3). If the reaction of the dianion would proceed via S_N2 only, 5-allylacenaphthene should be obtained as the only product. However, the reaction gives a mixture of products, in which 1-allylacenaphthene is the major substitution product. Because allyl bromide is more easily reduced than simple alkyl halides such as methyl iodide and (bromomethyl)cyclopropane, the reaction of **1** with allyl bromide might proceed via SET. In the SET reaction one electron is transferred from the dianion to allyl bromide (Scheme 1). In a concerted electron transfer-bond breaking mechanism, allyl bromide dissociates into an allyl radical and a bromide ion. The allyl radical and the resulting acenaphthylene radical anion will combine to a substituted acenaphthylene hydroanion. This anion can react a second time with allyl bromide (now via S_N2) or it can become protonated during work-up.

If the reaction of **1** with allyl bromide takes place via SET, the position at which substitution occurs, is not determined by the charge distribution and HOMO coefficients in the dianion but by those in the radical anion. In non-alternant PAH the most reactive position in the radical anion can be different from that in the dianion. The dianion reacts preferably at position 5, whereas the highest reactivity in the radical anion is found at position 1.[1] This was proven by the reaction of the radical anion and the dianion with water: the radical anion gave acenaphthene (1,2-dihydroacenaphthylene) as the only product, whereas the protonation product of the dianion is 1,5-dihydroacenaphthylene.[1] Because the reaction of **1** with allyl bromide gave predominantly substitution at position 1, it can be concluded that the radical anion was an intermediate and thus that SET plays a role in the mechanistic pathway. After the first substitution, the resulting 1-allyl-1-hydroacenaphthylene anion might react a second time. The most likely position for this second substitution is position 2, thus giving the 1,2-diallylacenaphthene. The formation of 5-allylacenaphthene **3b** might be the result of reaction via an S_N2 pathway or an SET reaction. It would be interesting to perform the reaction of **1** with allyl bromide in the presence of a radical scavenger in order to investigate the mechanism by which **3b** is formed (see Chapter 4). Compound **3d** might result from reaction of the 5-allyl-5-hydroacenaphthylene anion with a second equivalent of allyl bromide at position 1. Alternatively, the 1-allyl-1-hydroacenaphthylene anion might react also at position 5, resulting in **3d**. The latter pathway is less likely, because substitution at position 2, resulting in an aromatic naphthalene skeleton, is energetically more favorable.

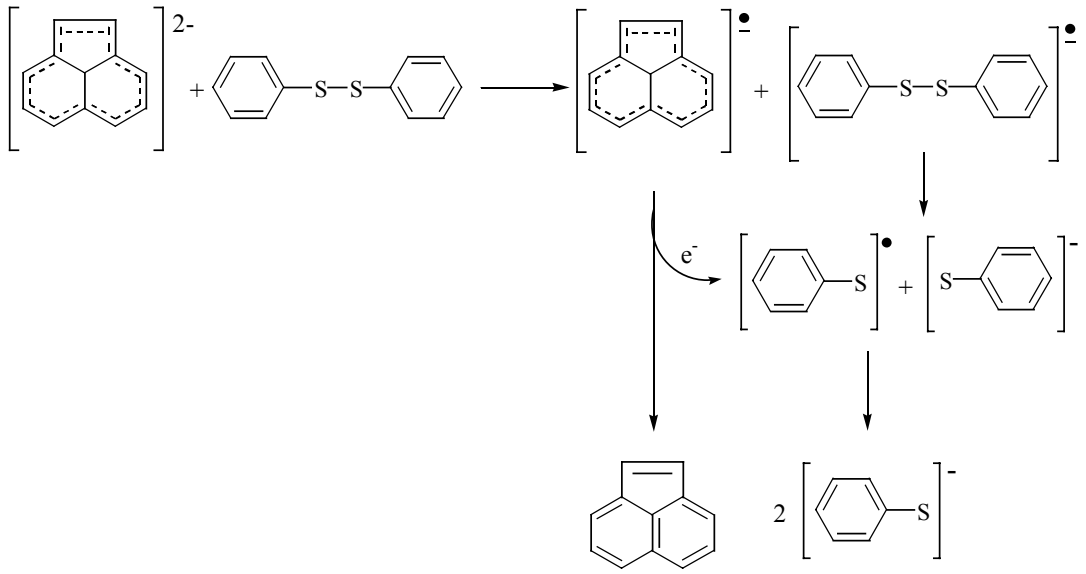
The occurrence of the SET mechanism was confirmed by the reaction of **1** with 3,3-dimethylallyl bromide. In the case of electron transfer the allyl radical now has two different reactive positions and thus may give rise to coupling products with the methyl groups at position 1 or at position 3 of the allyl chain (see Chapter 3). Two different methyl groups are indeed observed by NMR spectroscopy. Therefore, it can be concluded that SET does indeed play a role in the reaction of **1** with allylic bromides.

Bromoacetaldehyde diethylacetal is an electrophile which is known to react via electron transfer.[2,3] In the reaction with **1** a substitution pattern similar to that of allyl bromide is found.

Based on these results the observations of Neumann and Müllen can be understood.[4] These authors found that the reaction of the acenaphthylene dianion with 1,ω-dichloroalkanes was not regioselective, in contrast to the reaction with methyl iodide. The product distribution is similar to the one we found for the reaction of **1** with allyl bromide. Therefore, it seems likely that this reaction also proceeds via SET and thus that the regioselectivity is not determined by **1** but by the radical anion.

Reaction of the dianion with alkyl halides containing functional groups such as ethyl bromoacetate, however, results in oxidation of the dianion. This can be rationalised by the assumption that a double electron transfer is responsible for the conversion into the starting material. In Scheme 2 this double electron transfer is shown for the reaction of **1** with diphenyl

disulfide. Only a small percentage (<10%) of addition products was detected in reactions with these electrophiles.



***Scheme 2**: Double electron transfer from **1** to diphenyl disulfide.*

Reaction of **1** with bromobenzene gives a mixture of substitution products. Because bromobenzene cannot give an S_N2 reaction with nucleophiles, the mechanism must be different. The most important mechanism for nucleophilic aromatic substitution is addition-elimination. However, the presence of strongly electron-demanding groups is required to give a fast reaction. A second possibility is the benzyne mechanism. This substitution occurs on aryl halides that have no activating groups. For this reaction a very strong base, such as KNH_2, is required.[5] The acenaphthylene dianion might be strong enough to abstract a proton from bromobenzene. The resulting 5-hydroacenaphthylene anion will then react with benzyne, most likely at position 1. This reaction therefore does not explain the formation of a complex mixture of products. Next to a strong base, the acenaphthylene dianion is also a strong electron donor. Therefore, bromobenzene might be substituted via the $S_{RN}1$ mechanism.[6-9] This mechanism, depicted in eq 1-4, is initiated by electron transfer to substrate ArX from a suitable electron donor. This ET (eq 1) can occur under the influence of light,[10-13] electrochemically[14-16] or by free electrons.[17,18]

$$ArX + e^- \longrightarrow ArX^{\bullet -} \qquad (1)$$

$$ArX^{\bullet -} \longrightarrow Ar^{\bullet} + X^- \qquad (2)$$

$$Ar^{\bullet} + Nu^- \longrightarrow ArNu^{\bullet -} \qquad (3)$$

$$ArNu^{\bullet -} + ArX \longrightarrow ArNu + ArX^{\bullet -} \qquad (4)$$

The radical anion thus formed dissociates (eq 2) to give an aryl radical and a halide anion. The aryl radical combines with the nucleophile to form an adduct (eq 3), which is a radical anion. In a next step (eq 4) the extra electron is transferred to a haloarene and the resulting radical anion will continue the chain (eq 2 and eq 3). This chain process can be terminated by coupling of two radicals or by reduction of the adduct.[6,19] In the reaction of **1** with bromobenzene the dianion (A^{2-}) can act as the electron source. In the first step one electron is transferred to bromobenzene (eq 5) resulting in an acenaphthylene radical anion and a bromobenzene radical anion. The latter dissociates (eq 2) into a phenyl radical and a bromide anion. Then the acenaphthylene radical anion combines with the phenyl radical (eq 6). This anion ($Ar\text{-}A^-$) is protonated in the work-up procedure by water. In contrast to the chain process in the $S_{RN}1$ reaction, the reaction of **1** with bromobenzene is in principle a one-to-one reaction.

$$ArX + A^{2-} \longrightarrow ArX^{\bullet -} + A^{\bullet -} \qquad (5)$$

$$ArX^{\bullet -} \longrightarrow Ar^{\bullet} + X^- \qquad (2)$$

$$Ar^{\bullet} + A^{\bullet -} \longrightarrow Ar\text{-}A^- \qquad (6)$$

The position where the addition takes place depends on the properties of the acenaphthylene radical anion. There is an attractive MO interaction between the benzene radical and the carbanion nucleophile: the strongest interaction occurs at the nucleophilic position with the highest HOMO coefficient.[20] In the acenaphthylene radical anion the positions 1 (2) and 5 (6) are those with the highest SOMO coefficients. The relative rate of an $S_{RN}1$ reaction is not only controlled by the stability of the product radical ions but also by the strength of the incipient carbon-carbon bond.[21] This latter factor might also influence the substitution pattern.

Reaction of **1** with *para*-bromotoluene gave a similar substitution pattern as in the case of reaction with bromobenzene. In this case no oxidised products were detected. However, a product with mass 182 was found with GC-MS. This must be dimethylbiphenyl that is formed by coupling of two methylphenyl radicals. Normally, this coupling product is not observed in $S_{RN}1$ reactions, because of the low concentration in which it is present. In our reaction the concentration of toluene radicals is relatively high and thus this termination step will take place.

A third electrophile which cannot give S_N2 reaction is β-bromostyrene. With GC-MS one major addition product and traces of other mono- and disubstitution products are detected. Obviously, also in this case the reaction starts with electron transfer. In recent years Rappoport and co-workers have found that vinyl halides can react in an $S_{RN}1$ reaction.[22-25] They encountered, however, problems with side-reactions, such as addition-elimination. In the case of the reaction of **1** with bromostyrene

these side-reactions will probably not interfere with the $S_{RN}1$ reaction. Although GC-MS showed one major substitution product, the ^{1}H NMR spectrum was too complicated to identify the product. It might also be a mixture of isomers, which cannot be separated by GC.

6.4 Conclusions

The acenaphthylene dianion reacts with bromomethylcyclopropane via the S_N2 mechanism and this occurs selectively at position 5. The SET mechanism plays an important role in the reaction of **1** with allyl bromide. Due to the role of the acenaphthylene radical anion as reaction intermediate, a mixture of 1-allyl-, 5-allyl-, 1,2-diallyl- and 1,5-diallylacenaphthenes was obtained. The occurrence of the SET mechanism was confirmed by the reaction of **1** with 3,3-dimethylallyl bromide. A double electron transfer occurs if more readily reducible electrophiles, such as diphenyl disulfide and ethyl bromoacetate are used. Bromobenzene, *para*-bromotoluene and β-bromostyrene give an $S_{RN}1$-type reaction with **1** and complex product mixtures are obtained.

6.5 Experimental section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration over silica. The electrophiles were obtained from Acros, Aldrich and Merck and used without further purification. 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 ^{1}H 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 ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra.

Preparative GC was performed on an ATI Unicam 610 series gas chromatograph equipped with an SE 15% 3 m column with the following temperature profile: 10 min. 100°C, 10°C/min. to 160°C, 15 min. 160°C.

Mass spectra were recorded on a Finnigan MAT 900 mass spectrometer, equipped with a direct insertion probe (EI-MS, 70 eV) or on a Finnigan MAT ITD 700 (EI, 70 eV) coupled to a Packard 438A gas chromatograph equipped with a Chrompack 25 m fused silica column (CP-Sil-5CB; 0.25 mm i.d.) (GC-MS).

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, 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 0ºC, a deep green solution was obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70ºC and the electrophile (5 mmol) was added. The mixture was allowed to warm to room temperature and stirred for a further 30-60 minutes, after which period the reaction was quenched with water. Addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oils.

*Reaction of **1** with allyl bromide:*

To a solution of **1** (5 mmol), allyl bromide (0.43 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography a mixture of products was obtained (mass recovery more than 90%). This mixture was separated by preparative gas chromatography. Next to acenaphthene and acenaphthylene the following products were found: 1-allylacenaphthene **3a** (39%), 5-allylacenaphthene **3b** (21%), 1,2-diallylacenaphthene **3c** (17%), 1,5-diallylacenaphthene **3d** (12%),1-allylacenaphthylene **3e** (5%) and another diallylacenaphthene **3f** (6%) (Figure 1). **3e** and **3f** could not be characterised by NMR. From **3e** no GC-MS spectrum was measured.

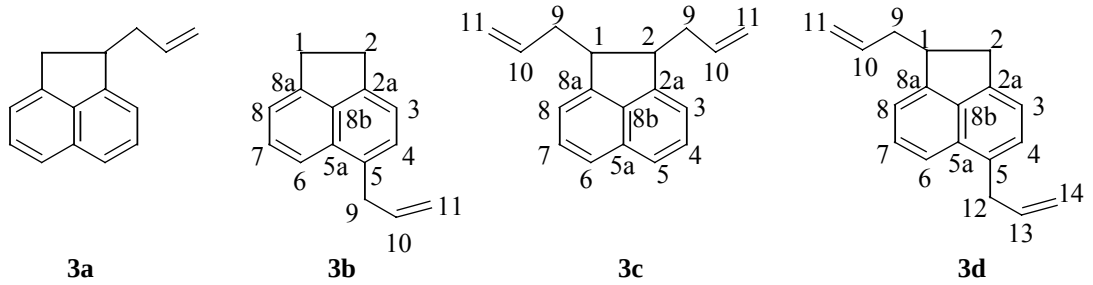


***Figure 1**: Isolated products from the reaction of **1** with allyl bromide.*

1-Allylacenaphthene (**3a**)*:see Chapter 3*

5-Allylacenaphthene (**3b**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.69 (ddt, $J_{6,7}$ = 8.3, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.45 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.9**,** 1 H, H-7), 7.27 (ddt, $J_{7,8}$ = 6.9, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.27 (d, $J_{3,4}$ = 6.9, H-4), 7.21 (dt, $J_{3,4}$ = 6.9, $J_{2,3}$, 1 H, H-3), 6.09 (m, 1 H, H-10), 5.11 (m, 1 H, H-11), 5.07 (m, 1 H, H-11'), 3.76 (ddd, $J_{9,10}$ = 6.3, $J_{9,11}$, $J_{9,11'}$, 2 H, H-9), 3.38-3.36 (m, 4 H, H-1 and H-2), $J_{1,6}$, $J_{1,8}$, $J_{6,8}$, $J_{2,3}$, $J_{9,11}$, $J_{9,11'}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) δ: 137.3 (C-10), 127.6 (C-7), 127.5 (C-4), 119.4 (C-6), 119.0 (C-3 and C-8), 115.7 (C-11), 36.4 (C-9), 30.5 (C-1 or C-2), 29.8 (C-1 or C-2), quaternary C's not observed.
GC-MS m/z (%): 194 (100), 179 (11), 165 (13), 153 (5).

1,2-Diallylacenaphthene (**3c**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.62 (d, $J_{4,5}$ = $J_{6,7}$ = 8.2, 2 H, H-5 and H-6), 7.46 (dd, $J_{4,5}$ = $J_{6,7}$ = 8.2, $J_{3,4}$ = $J_{7,8}$ = 6.9**,** 2 H, H-4 and H-7), 7.28 (d, $J_{3,4}$ = $J_{7,8}$ = 6.9, 2 H, H-3 and H-8), 5.84 (m, 2 H, H-10), 5.09 (m, 2 H, H-11), 5.05 (m, 2 H, H-11'), 3.45 (t, $J_{1,9}$ = $J_{2.9}$ = 5.8, 2 H, H-1 and H-2), 2.54 (m, $J_{9,10}$ = 6.3, $J_{9,11}$, $J_{9,11'}$, 4 H, H-9).
^{13}C NMR ($CDCl_3$) δ: 137.3 (C-10), 128.6 (C-4 and C-7), 123.6 (C-5 and C-6), 120.0 (C-3 and C-8), 117.5 (C-11), 49.7 (C-1 and C-2), 41.2 (C-9), quaternary C's not observed.
GC-MS m/z (%): 234 (48), 193 (100), 178 (21), 165 (23), 152 (4).

1,5-Diallylacenaphthene (**3d**)

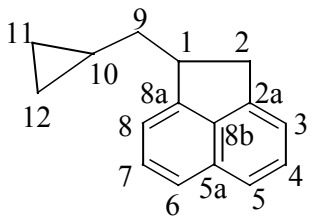
^{1}H NMR ($CDCl_3$, TMS) δ: 7.72 (d, $J_{6,7}$ = 8.3, 1 H, H-6), 7.48 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.9, 1 H, H-7), 7.31-7.18 (m, 3 H, H-3, H-4 and H-8), 6.09 (m, 1 H, H-13), 5.89 (m, 1 H, H-10), 5.15-5.05 (m, 4 H, H-11 and H-14), 3.79-3.74 (m, 3 H, H-1 and H-12), 3.50 (dd, $J_{2,2'}$ = -16.9, $J_{1,2}$ = 7.8, 1 H, H-2), 3.06 (dd, $J_{2,2'}$ = -16.9, $J_{1,2'}$ = 2.9, 1 H, H-2'), 2.66 (m, 1 H, H-9), 2.42 (m, 1 H, H-9').
GC-MS m/z (%): 234 (100), 193 (73), 178 (12), 165 (18).

Third disubstituted product (**3f**)

GC-MS m/z (%): 234 (68), 193 (100), 178 (21), 165 (24), 152 (5).

*Reaction of **1** with (bromomethyl)cyclopropane:*

To a solution of **1** (3 mmol) (bromomethyl)cyclopropane (0.29 ml, 3 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography 5-(cyclopropylmethyl)acenaphthene was obtained as the major product (>90%). GC-MS analysis showed that also some acenaphthene and 5-(cyclopropylmethyl)acenaphthylene were present.



5-(Cyclopropylmethyl)-acenaphthene (**4**)

^{1}H NMR ($CDCl_3$, TMS) δ: 7.69 (ddt, $J_{6,7}$ = 8.3, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.45 (dd, $J_{6,7}$ = 8.3, $J_{7,8}$ = 6.9, 1 H, H-7), 7.27 (ddt, $J_{7,8}$ = 6.9, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.27 (d, $J_{3,4}$ = 6.9, H-4), 7.21 (dt, $J_{3,4}$ = 6.9, $J_{2,3}$, 1 H, H-3), 3.38-3.36 (m, 4 H, H-1 and H-2), 2.91 (d, $J_{9,10}$ = 6.2, 2 H, H-9), 1.14 (m, 1 H, H-10), 0.53 (m, 2 H, H-11/12), 0.25 (m, 2 H, H-11/12).

^{13}C NMR ($CDCl_3$) δ: 146.3 (C-2a or C-8a), 143.9 (C-2a or C-8a), 133.8 (C-5a), 126.9 (C-4 and C-7), 119.3 (C-6), 119.0 (C-3 or C-8), 118.9 (C-3 or C-8), 36.2 (C-9), 30.5 (C-1 or C-2), 29.8 (C-1 or C-2), 11.3 (C-10), 5.1 (C-11 or C-12), 5.0 (C-11 or C-12).

Exact mass calculated for $C_{16}H_{16}$: 208.1252 m/z; found: 208.1252. MS m/z (%): 208 (100), 193 (23), 179 (20), 167 (74), 165 (60), 152 (31)139 (2), 115 (2), 89 (5).

*Reaction of **1** with bromobenzene:*

To a solution of **1** (5 mmol), bromobenzene (0.537 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography a mixture of phenylacenaphth(yl)enes was obtained (yield: 60-90%). GC-MS analysis showed 6 products in the following ratio: A (20%), B (13%), C (18%), D (7%), E (19%), F (23%)

A: GC-MS m/z (%): 230 (100), 152 (22).
B: GC-MS m/z (%): 228 (100), 202 (11), 113(10).
C: GC-MS m/z (%): 230 (100), 202 (6), 153 (8), 113 (5).
D: GC-MS m/z (%): 228 (100), 113 (11).
E: GC-MS m/z (%): 230 (100), 215 (15), 153 (7).
F: GC-MS m/z (%): 308/310 (100/92), 229 (70), 153 (8), 113 (13), 101 (10).

*Reaction of **1** with para-bromotoluene:*

To a solution of **1** (5 mmol), *p*-bromotoluene (0.62 ml, 5 mmol) was added at -60ºC and the solution was stirred for a further 30 minutes. After normal work-up and purification by silica gel column chromatography a mixture of methylphenylated acenaphthenes was obtained. GC-MS analysis showed next to dimethylbiphenyl four products in the following ratio: A (26%), B (15%), C (35%), D (24%)

A: GC-MS m/z (%): 244 (100), 229 (96), 152 (58).
B: GC-MS m/z (%): 244 (100), 229 (25), 153(12).
C: GC-MS m/z (%): 244 (100), 229 (40), 152 (5).
D: GC-MS m/z (%): 322/324 (100/93), 243 (38), 228 (41), 152 (4).

*Reaction of **1** with E/Z bromostyrene:*

To a solution of **1** (3 mmol), E/Z β-bromostyrene (0.40 ml, 5 mmol) was added at -60ºC and the solution was stirred for 30 minutes. After normal work-up and purification by silica gel column chromatography, styrylacenaphthene was obtained. GC-MS analysis showed one major product.
GC-MS m/z (%): 256 (43), 165 (100), 91 (8), 43 (10).

6.6 References

1 C.V. Ristagno, R.G. Lawler *Tetrahedron Lett.* **1973**, 159-162
2 G.M. Stork *J. Am. Chem. Soc.* **1973**, *95*, 2014
3 M. Kuhn *J. Prakt. Chem.* **1940**, *156*, 103
4 G. Neumann, K. Müllen *Chimia* **1985**, *39*, 275-276
5 J. March *Advanced Organic Chemistry* **1985** 3rd ed. J. Wiley and Sons, New York
6 R.K. Norris in *Comprehensive Organic Synthesis*, **1991**, Eds. B. Trost , I. Fleming, Pergamon Press, Oxfort, Vol. 4, Chapter 2.2
7 J.E. Swartz, J.F. Bunnett *J. Org. Chem.* **1979**, *44*, 340-346
8 R.A. Rossi, J.F. Bunnett *J. Org. Chem.* **1973**, *38*, 3020-3025
9 R.A. Rossi, J.F. Bunnett *J. Am. Chem. Soc.* **1974**, *96*, 112-117
10 R.A. Rossi, R.H. de Rossi, A.F. López *J. Org. Chem.* **1976**, *41*, 3371-3373
11 J.F. Bunnett, X. Creary *J. Org. Chem.* **1974**, *39*, 3171-3174
12 M.P. Moon, A.P. Komin, J.F. Wolfe *J. Org. Chem.* **1983**, *48*, 2392-2399
13 R.A. Rossi, R.A. Alonso *J. Org. Chem.* **1980**, *45*, 1239-1241
14 C. Amatore, M. Gareil, M.A. Oturan, J. Pinson, J.-M. Savéant, A. Thiébault *J. Org. Chem.* **1986**, *51*, 3757-3761

15 C. Amatore, C. Combellas, S. Robveille, J.-M. Savéant, A. Thiébault *J. Am. Chem. Soc.* **1986**, *108*, 4754-4760
16 P. Boy, C. Combellas, C. Suba, A. Thiébault *J. Org. Chem.* **1994**, *59*, 4482-4489
17 R.A. Rossi, R.H. de Rossi, A.F. López *J. Am. Chem. Soc.* **1976**, *98*, 1252-1257
18 J.F. Bunnett, J.E. Sundberg *Chem. Pharm. Bull.* **1975**, *23*, 2620-2628
19 R. Ettayeb, J.-M. Savéant, A. Thiébault *J. Am. Chem. Soc.* **1992**, *114*, 10990-10991
20 R.A. Rossi, R.H. de Rossi, A.F. López *J. Org. Chem.* **1976**, *41*, 3367-3371
21 L.M. Tolbert, S. Siddiqui *J. Org. Chem.* **1984**, *49*, 1744-1751
22 C. Galli, P. Gentili, Z. Rappoport *J. Org. Chem.* **1994**, *59*, 6786-6795
23 C. Amatore, C. Galli, P. Gentili, A. Guarnieri, E. Schottland, Z. Rappoport *J. Chem. Soc., Perkin Trans. 2* **1995**, 2341-2350
24 C. Galli, P. Gentili, A. Guarnieri, Z. Rappoport *J. Org. Chem.* **1996**, *61*, 8878-8884
25 A.N. Santiago, G. Lassaga, Z. Rappoport, R.A. Rossi *J. Org. Chem.* **1996**, *61*, 1125-1128