Part I

Reductive alkylation of

Acenaphthylene

2

The acenaphthylene dianion and 5-hydroacenaphthylene anion

2.1 Introduction

The investigation of the reactivity of the acenaphthylene dianion starts with the use of simple electrophiles: a proton donor (methanol and/or water) and methyl iodide. With these reagents the reactive positions in the anionic intermediates can be determined. The results will be correlated to NMR data and compared to the results of quantum chemical calculations. In these calculations, the charge and HOMO coefficient distributions in the dianion and the hydroanion are used to predict the most reactive positions. Because reactions of anions of PAH with electrophiles normally are fast and thus have an early transition state, this initial state approximation might give a good insight in the reaction process.

2.2 Results

2.2.1 Reactions with electrophiles

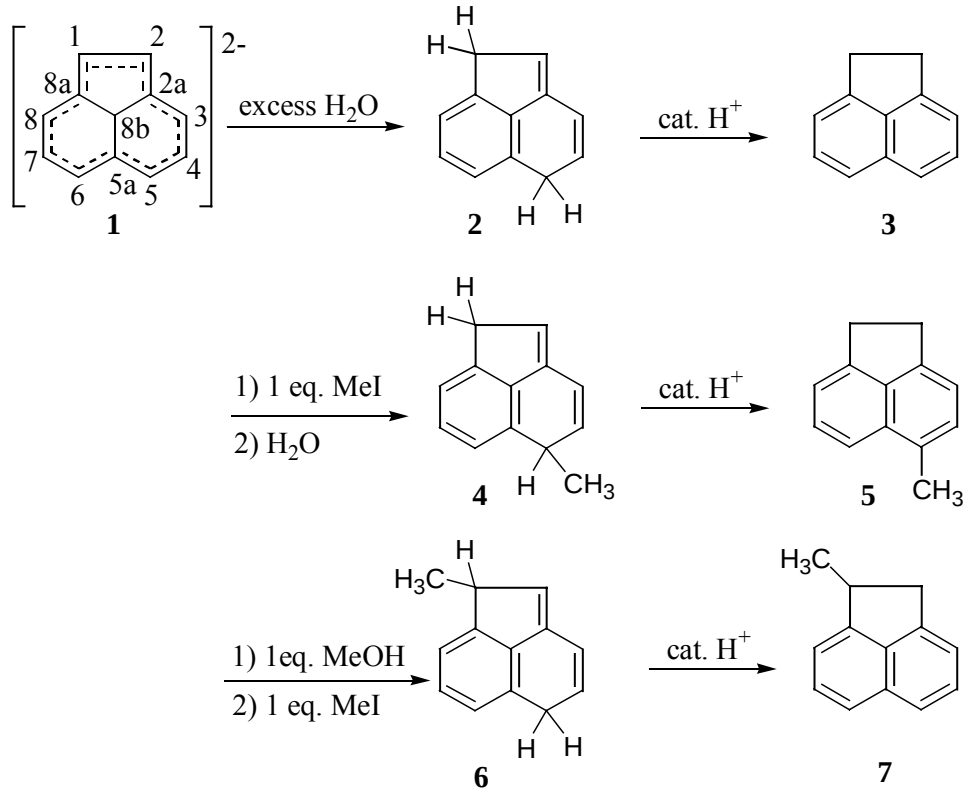
The dianion of acenaphthylene was prepared by dissolving the hydrocarbon (0.5-5 g) and 2.2 equivalents of sodium in anhydrous THF, and exposing the solution to ultrasonic vibration. Within 3-5 hours the colour of the solution turned deep green, indicating that the dianion (**1**) (Scheme 1) had been formed.[1]

The solution of **1** was treated at -70ºC with excess water and stirred for 15 minutes at room temperature. After extraction with light petroleum (boiling range 40-60ºC) and work-up, 1,5-dihydroacenaphthylene (**2**) was obtained quantitatively. Upon dissolving **2** in acetone and adding a few drops of concentrated HCl, a rearrangement took place, resulting in the formation of the stable acenaphthene (**3**) in 98% yield (Scheme 1).

In the next experiment one equivalent of methyl iodide was added to **1** at -70ºC, and the mixture was stirred for 30 minutes at room temperature. The solution was again cooled to –70ºC and excess water was added. 1,5-Dihydro-5-methylacenaphthylene (**4**) was isolated after extraction with light petroleum (boiling range 40-60ºC) and work-up in more than 95% yield. This compound appeared to be unstable upon storage at room temperature; under slightly acidic conditions it rearranges to 5-methylacenaphthene (**5**) quantitatively (Scheme 1).

If the sequence of addition of the electrophiles to the dianion was reversed i.e., with the addition of one equivalent of proton donor (methanol) followed by one equivalent of methyl iodide, the procedure described above yielded 1,5-dihydro-1-methylacenaphthylene (**6**) almost quantitatively. 1-Methylacenaphthene (**7**) was obtained after exposure of the product to slightly acidic conditions (Scheme 1).

When two equivalents of methyl iodide, or one equivalent of ethyl iodide followed by one equivalent of methyl iodide, were added to the acenaphthylene dianion, a mixture of mono-, di- and multisubstituted products was obtained.



***Scheme 1**: Reaction of the acenaphthylene dianion with electrophiles.*

2.2.2 ^{1}H and ^{13}C NMR spectroscopy

*Acenaphthylene dianion (**1**)*

The dianion of acenaphthylene was prepared in THF-d_8 in an NMR tube, using the procedure described by Van Dijk (See experimental).[2] The measured spectra (^{1}H and ^{13}C) were nearly identical to those reported previously.[1,3-8] Small deviations in chemical shifts can be ascribed to differences in conditions. The spectra were assigned using H-H and C-H COSY techniques. The signals in the ^{1}H NMR spectrum are broad. This might be due to the temperature (20ºC) and the

high concentration. The protons H-5 and H-6 have the highest chemical shift value (5.93 ppm) and this means that a large amount of charge is located at C-5 and C-6.

The signals in the ^{13}C NMR spectrum are very sharp, indicating that no more radical anion is present. It can also be concluded that the acenaphthylene dianion is a diamagnetic and symmetric particle. The ^{13}C NMR shift values strongly depend on the temperature and on the counter ion.[4,5,8] At room temperature the signals of C-5/C-6 appear at the highest field (82.6 ppm), followed by C-1/C-2 (85.9 ppm) and C-3/C-8 (96.9 ppm). The average shift over all carbon atoms due to the lower temperature was 0.34 ppm per carbon atom downfield. Lowering of the temperature to -80ºC results in a downfield shift for C-5/C-6 to 83.7 ppm whereas C-1/C-2 undergo an upfield shift to 84.7 ppm.

***Table 1**: ^{13}C NMR chemical shifts of **1** and acenaphthylene (ANY) in ppm, the difference in chemical shift between neutral and dianion and the charge derived from this difference.*

Carbon atom	δ ^{13}C (20ºC)	δ ^{13}C (-80ºC)	δ ^{13}C ANY	δ (**1**) - δ (ANY)	charge
1,2	85.9	84.7	129.7	-43.8	-0.36
3,8	96.9	96.1	128.7	-31.8	-0.26
4,7	126.7	126.9	124.3	+2.4	+0.02
5,6	82.6	83.4	127.9	-45.3	-0.38
2a, 8a	123.4	122.9	140.0	-16.6	-0.14
5a	149.2	148.6	128.4	+20.8	+0.17
8b	137.7	137.0	127.4	+10.3	+0.09

The ^{13}C chemical shifts can be used as measure for the charge distribution in the acenaphthylene dianion.[8] The shielding of the carbon atoms is supposed to vary linearly with the corresponding π-electron density (see Chapter 1). The ^{13}C NMR signals are paratropically shifted with respect to the signals of the neutral compound by a total of 239.1 ppm. This is considerably less than would be expected for the induction by two electrons (320 ppm). A possible explanation for the low K_c is a reduced average excitation energy and consequently an increased paramagnetic shielding in the dianion.[4] This might also be the explanation for the variation of K_c with different combinations of cation, solvent and temperature. Because also other PAH gave variations of K_c, system-specific K_c-values should be used.[4]

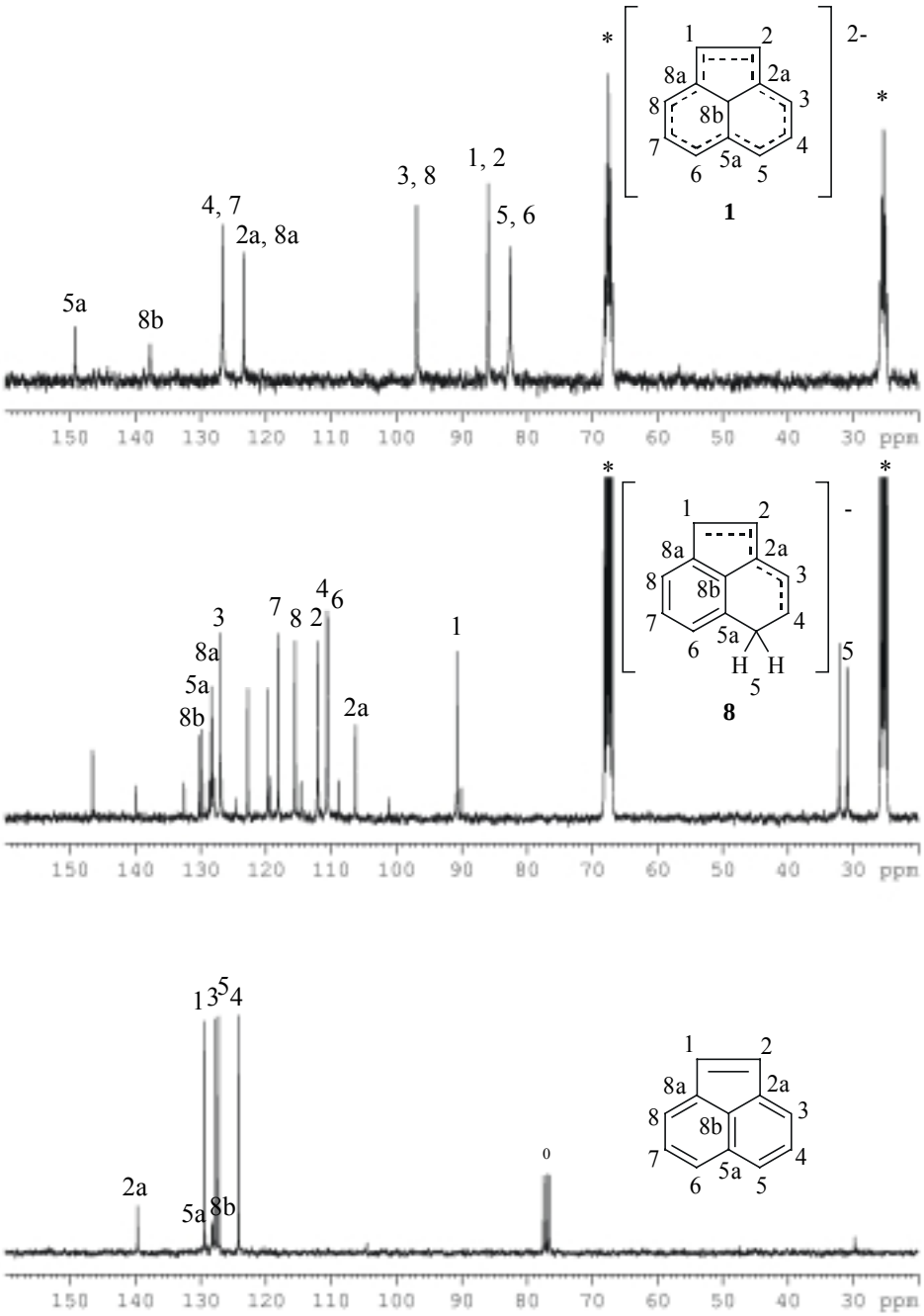


Figure 1: *^{13}C NMR spectra of the acenaphthylene dianion (**1**), the 5-hydroacenaphthylene anion (**8**) and acenaphthylene (75 MHz, 20ºC, * = THF, º = $CDCl_3$, the spectrum of **8** contains some acenaphthene).*

The difference in chemical shifts between the neutral and dianionic system was used to estimate the charge on the carbon atoms (Table 1, column 6). Despite the fact that the five-membered ring tends to attract the charge to its carbon atoms it appears that the highest charge is found at carbon atoms 5 and 6. Also a high charge is located at carbon atoms 1 and 2, although less than expected.[7] The carbon atoms 4 and 7 are predicted to bear even a positive charge. The carbon atoms with the highest charge are the ones from which the ^{13}C NMR shifts are most affected by the temperature. More detailed NMR studies showed that in the case of lithium one cation is linked to the five-membered ring while the other appears as a solvated ion at positions 5 and 6.[8]

*5-Hydroacenaphthylene anion (**8**)*

The 5-hydroacenaphthylene anion (**8**) was prepared in THF-d_8 and transferred into an NMR tube. The measured spectra (^1H and ^{13}C) were similar to those recorded by Müllen and co-workers.[6] The small deviations in chemical shifts can be ascribed to differences in temperature, counter ion (Na *versus* Li), proton donor (methanol *versus* ammonia) and concentration. The ^1H and ^{13}C NMR spectra were assigned completely using H-H and C-H inverse COSY techniques. The ^1H spectrum (see experimental section) consists of 7 broad signals forming an ABC pattern for protons H-6, H-7 and H-8, an AB pattern for H-1 and H-2 and an ABX_2 pattern for H-3, H-4 and H-5. H-6 and H-8 could be distinguished by measuring NOEDIFF.

From the chemical shifts in the ^{13}C NMR spectrum (Table 3) the charge distribution in the hydroanion can be determined.[8] It is obvious that the highest charge is located at C-1. However, attention should be paid to C-2a, which has a noteworthy shift upfield, indicating that also a substantial amount of charge is located at this carbon atom.

Although in ^1H NMR H-4 is found at relatively high field (4.78 ppm), the ^{13}C NMR chemical shift indicates that much less charge is located at C-4 than at C-1. Because in ^1H NMR other factors such as ring current contribute to the shielding of hydrogens, an indication of the charge distribution should preferably be based on ^{13}C NMR.Furthermore it should be noted that C-3 appears at very low field and thus has very little negative charge or even is positively charged. This is in accordance with the charge alternation concept as proposed by Rabinovitz and co-workers.[7]

*1,5-Dihydroacenaphthylene (**2**), 1,5-dihydro-5-methylacenaphthylene (**4**) and 1,5-dihydro-1-methylacenaphthylene (**6**)*

The ^1H NMR spectrum of 1,5-dihydroacenaphthylene (**2**) was identical to that reported earlier.[9]

The ^1H NMR spectrum of 1,5-dihydro-5-methylacenaphthylene (**4**) closely resembles that of **2** and consists of an ABX and an $ABMX_3$ pattern for the non-aromatic part of the molecule and an ABC pattern for the three aromatic protons. The methyl group shows couplings with H-5 and H-4.

The ^{1}H NMR spectrum of 1,5-dihydro-1-methylacenaphthylene (**6**) is similar to the spectrum of 1,5-dihydro-5-methylacenaphthylene (**4**). The non-aromatic protons gave an ABX_2 and an AMX_3 pattern. In this case the methyl group gave only coupling with H-1.

*5-Methylacenaphthene (**5**) and 1-methylacenaphthene (**7**)*

After rearrangement of **4**, the methyl group has become benzylic and shifts to 2.61 ppm. The rest of the spectrum of 5-methylacenaphthene (**5**) closely resembles that of acenaphthene.

The aromatic part of the ^{1}H NMR spectrum of 1-methylacenaphthene (**7**) is almost identical to that of acenaphthene. The methyl group induces chirality at C-1. The protons at C-2 can be distinguished on the basis of their different couplings with H-1; the H-H cis-coupling is 8.0 Hz whereas the trans-coupling is 3.2 Hz.

2.2.3 *Ab initio* calculations

Quantum chemical calculations can give additional information for the understanding of chemical reactions and NMR spectra. Therefore, the charge distribution, the HOMO coefficients and the shielding constants were calculated with *ab initio* methods for the acenaphthylene dianion (**1**) and the 5-hydroacenaphthylene anion (**8**). The calculations were carried out with the GAUSSIAN 94 suites of programs.[10] The geometries were fully optimised without symmetry restriction at the HF level by using the 6-31G(d,p) basis set, and characterised by frequency calculations. The shielding constants for the ^{13}C NMR spectrum were calculated and they correlate well with the experimental data.

The experimental and calculated ^{13}C NMR chemical shifts as well as the Mulliken sum charges (hydrogens included) and the HOMO coefficients are given for the acenaphthylene dianion(**1**) and for the 5-hydroacenaphthylene anion (**8**) in Table 2 and in Table 3, respectively. It should, however, be realised that several factors, such as counter ion and solvent, have been neglected in the calculations. Therefore, the calculations should only be ussed as an indication of the most reactive positions. A pictorial representation is given in Figure 2.

***Table 2**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), Mulliken sum charge distribution and HOMO coefficients of acenaphthylene dianion (**1**).*

Carbon atom	δ ^{13}C (20ºC)	δ ^{13}C (calc.)	Charge	HOMO
1,2	85.9	76.4	-0.302	0.323
3,8	96.9	86.2	-0.254	0.354
4,7	126.7	124.8	-0.086	0.124
5,6	82.6	67.0	-0.356	-0.425
2a, 8a	123.4	118.2	+0.022	-0.273
5a	149.2	152.1	+0.171	0.000
8b	137.7	127.1	-0.219	0.000

***Table 3**: Experimental and calculated ^{13}C NMR chemical shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), Mulliken sum charge distribution and HOMO coefficients of 5-hydroacenaphthylene anion (**8**).*

Carbon atom	δ ^{13}C (20ºC)	δ ^{13}C (calc.)	Charge	HOMO
1	90.7	84.0	-0.207	-0.275
2	112.1	114.4	-0.099	0.033
3	127.0	130.7	+0.028	-0.047
4	110.6	96.7	-0.168	-0.210
5	32.1	27.4	-0.016	0.049
6	110.5	104.0	-0.159	-0.136
7	118.1	111.0	-0.092	0.123
8	115.5	111.8	-0.092	0.144
2a	106.2	93.0	-0.123	0.303
5a	129.7	126.3	+0.028	-0.136
8a	128.2	124.9	+0.080	-0.115
8b	130.3	126.4	-0.109	0.088

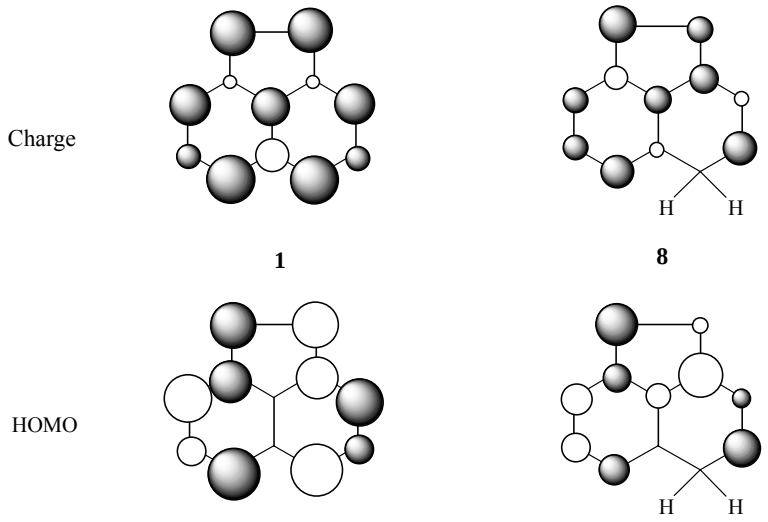


***Figure 2**: Charge distribution and HOMO coefficients of dianion **1** and hydroanion **8**.*

2.3 Discussion

The dianion of acenaphthylene can be prepared under Birch reduction conditions, using an alkali metal in a mixture of liquid ammonia and THF.[5,6,11] Using lithium in this reduction results in protonation of the acenaphthylene dianion by the solvent. To avoid this, the dianion **1** can better be prepared using pure THF as solvent. Efficient electron transfer from sodium to the PAH can be accomplished by using metal mirrors. A more convenient procedure uses ultrasonic vibration to accelerate the electron transfer.[4,12] We could perform the reduction of acenaphthylene to acenaphthene via its dianion on 10 gram scale using this procedure.

Experiments in which **1** is treated with a proton donor (hard electrophile) show that the first equivalent of proton reacts at position 5, resulting in the 5-hydroacenaphthylene anion **8**. This is subsequently protonated at position 1, resulting in 1,5-dihydroacenaphthylene (**2**).[9,13,14] Methyl iodide (soft electrophile) also reacts selectively at position 5 of **1**. Protonation of the resulting anion gives 1,5-dihydro-5-methylacenaphthylene (**4**) almost quantitatively. No dimethyl derivatives were obtained. A similar experiment was performed by Müllen and co-workers. They obtained, after dehydrogenation, 5-methylacenaphthylene as the sole product.[11] The high selectivity in the alkylation of the dianion provides a simple synthesis for 5-alkylated acenaphthenes and acenaphthylenes.

If the reaction of the acenaphthylene dianion (**1**) with methyl iodide proceeds via the S_N2 mechanism, the reaction is expected to proceed at the carbon with the highest charge and a high HOMO coefficient. The charge distribution in the acenaphthylene dianion can be derived from the differences in chemical shifts in the ^{13}C NMR spectrum of **1** with respect to that of neutral

acenaphthylene (Table 1). C-5 and C-6 are the carbon atoms with the largest upfield shift and thus the carbons with the highest charge. The calculated chemical shift values correlate very well with the experimental data. The *ab initio* calculations showed that the highest charge density and the highest HOMO-coefficient are located at C-5 (Table 2, Figure 2). This is in accordance with the ^{13}C NMR spectrum and the observed reactivity at position 5.

In the crystal structure of **1** the bond lengths differ for both sides of the molecule.[15] In solution, NMR gives no evidence for the existence of more than one species. So if there is an equilibrium between the different structures, this is so fast that they cannot be distinguished by NMR. The calculations give a fully symmetric structure for **1**, indicating that opposite carbons are identical. Remarkable is that the C-3-C-4 bond is rather short (1.37 Å) and has a high bond order (1.62). A second high bond order is found for C-2-C-2a (1.61), although this bond is not very short (1.40 Å). These high bond orders disfavour the reactivity at positions 1 (2) and 3 (8), and thus direct the substitution to take place at carbon atom 5 (6).

Reversal of the sequence of addition of methyl iodide and proton donor to the dianion, thus first one equivalent of methanol followed by one equivalent of methyl iodide, leads to protonation at position 5, giving the 5-hydroacenaphthylene anion (**8**), which in turn is methylated at position 1.

Similarly, the selectivity of the 5-hydroacenaphthylene anion (**8**) in the reaction with protons and methyl iodide can be explained by the presence of the highest charge and a high HOMO coefficient at C-1 (Table 3, Figure 2). From the ^{13}C chemical shifts it can be concluded that C-1 has the highest charge. *Ab initio* calculations predict the order of the chemical shifts very well (Table 3). Although C-2a has a very high HOMO coefficient, no reaction takes place at this position. This might be due to the smaller amount of charge at C-2a and the fact that quaternary centres are formed more difficultly in S_N2 reactions. The calculated high bond order (1.66) and the short bond length of the C-3-C-4 bond (1.34 Å) indicate that the C-3-C-4 bond already has a considerable amount of double bond character before interaction with the electrophile and this might cause the low reactivity of C-4 towards electrophiles. Based on the ^{13}C NMR spectrum and the quantum chemical calculations, the 5-hydroacenaphthylene anion (**8**) can be considered as a combination of a phenyl ring and a pentadienyl anion.

Both substituted 1,5-dihydroacenaphthylenes rearrange under acidic conditions to the corresponding acenaphthene derivatives. These structures have a higher degree of aromaticity and are therefore more stable.

Experiments have been reported in which two equivalents of electrophiles (D_2O, methyl iodide, CO_2, benzophenone) in the reaction with **1** yielded 1,5-disubstituted products exclusively.[16,17] The procedure described in this chapter was used to introduce two alkyl groups selectively at positions 1 and 5 in acenaphthylene. However, NMR spectroscopy showed that the reaction of **1** with two equivalents of methyl iodide led to a complex mixture of mono-, di- and polysubstituted products. Similar results were obtained for the reaction of **1** with two different electrophiles, e.g. ethyl iodide

followed by methyl iodide. The aselectivity of the reaction may have been the result of equilibration between products and reactants: e.g., 1,5-dihydro-1,5-dimethylacenaphthylene may transfer a proton to 5-hydro-5-methylacenaphthylene anion, to give a disubstituted hydroanion and a monosubstituted product (see Chapter 3). Another possibility might be that the methyl group at position 5 in the hydroanion does not affect the reactivity of the hydroanion towards protons, but does so towards alkyl halides. A third explanation for the difference with the literature data might be the advance in spectroscopic techniques, which enabled us to discriminate between mono- and polysubstituted products.

2.4 Conclusions

The dianion of acenaphthylene can easily be prepared on gram scale in THF, using ultrasonic vibration to activate the sodium. This dianion can be substituted with alkyl halides selectively at positions 1 or 5, depending on the sequence of addition of electrophiles. The resulting 1- or 5-substituted 1,5-dihydroacenaphthylenes rearrange under slightly acidic conditions to the corresponding acenaphthenes. The reactive positions in the acenaphthylene dianion and the 5-hydroacenaphthylene anion correlate well with the results of *ab initio* calculations and with the ^{13}C NMR data.

2.5 Experimental section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration over silica. Methyl iodide was obtained from Acros 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.

Reduction of acenaphthylene:

Into a dry 250 ml three-necked round-bottomed flask THF (125 ml) was distilled under an atmosphere of argon. Acenaphthylene (0.761 grams, 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-nitrogen bath to -70ºC and water was added. The colour of the mixture changed via red to yellow-brown. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. Addition of light petroleum (boiling range 40-60ºC), extraction with water, washing with brine, drying over $MgSO_4$ and the evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. Immediate analysis by NMR spectroscopy showed mainly 1,5-dihydroacenaphthylene.[9] This product was not stable to air and could, with a small amount of HCl in acetone, easily be converted into acenaphthene (Yield: 98%).

1,5-Dihydroacenaphthylene

^{1}H NMR ($CDCl_3$, TMS) δ 7.28 (d, $J_{7,8}$ = 7.2, 1H, H-8), 7.15 (dd, $J_{7,8}$ = 7.2, $J_{6,7}$ = 7.6, 1H, H-7), 7.04 (d, $J_{6,7}$ = 7.6, 1H, H-6), 6.59 (dt, $J_{3,4}$ = 10.0, $J_{3,5}$ = 2.4, 1H, H-3), 6.03 (dt, $J_{3,4}$ = 10.0, $J_{4,5}$ = 3.8, 1H, H-4), 5.95 (t, $J_{1,2}$ = 2.2, 1H, H-2), 3.70 (dd, $J_{4,5}$ = 3.8, $J_{3,5}$ = 2.4, 2H, H-5), 3.47 (d, $J_{1,2}$ = 2.2, 2H, H-1).

Reaction of the acenaphthylene dianion with methyl iodide:

According to the procedure described above, acenaphthylene (0.761 g, 5 mmol) was converted into the dianion and treated with methyl iodide (0.311 ml, 5 mmol) at -70°C. After stirring for 15 minutes at room temperature, the mixture was cooled again and quenched with water. After extraction, 1,5-dihydro-5-methylacenaphthylene was obtained in more thatn 95% yield.

1,5-Dihydro-5-methylacenaphthylene

^{1}H NMR ($CDCl_3$, TMS) δ 7.24-7.14 (m, 3H, H-6, H-7, H-8), 6.50 (dd, $J_{3,4}$ = 10.0, $J_{3,2}$ = 6.0, 1H, H-3), 5.95-5.90 (m, 2H, H-2, H-4), 3.65 (m, 1H, H-5), 3.45-3.43 (m, 2H, H-1), 1.30 (dd, $J_{Me,5}$ = 7.6, $J_{Me,4}$ = 2.6, 3H, CH_3).

Rearrangement to 5-methylacenaphthene was achieved by stirring for two hours in acetone with a few drops of HCl. The conversion was complete and 5-methylacenaphthene was isolated after extraction with light petroleum (boiling range 40-60ºC), drying over $MgSO_4$ and concentration quantitatively.

5-Methylacenaphthene

^{1}H NMR ($CDCl_3$, TMS) δ 7.64 (dd, $J_{6,7}$ = 8.3, $J_{6,8}$ = 0.9, 1H, H-6), 7.45 (dd, $J_{7,6}$ = 8.3, $J_{7,8}$ = 6.8, 1H, H-7), 7.27 (dd, $J_{8,7}$ = 6.8, $J_{8,6}$ = 0.8, 1H, H-8), 7.23 (dd, $J_{3,4}$ = 6.9, $J_{3,2}$ = 0.8, H-3), 7.15 (dd, $J_{3,4}$ = 7.0, $J_{4,Me}$ = 1.3, H-4), 3.39-3.31 (m, 4H, H-1, H-2), 2.61 (d, $J_{Me,4}$ = 0.9, CH_3).

^{13}C NMR ($CDCl_3$) δ 146.2 (C-2a or C-8a), 143.7 (C-2a or C-8a), 139.0 (C-8b), 129.8 (C-5a), 129.8 (C-3), 127.8 (C-7), 119.5 (C-6), 119.0 (C4 or C8), 118.9 (C4 or C8), 30.6 (C1 or C2), 29.8 (C1 or C2), 17.9 (CH_3), C-5 was not observed.

Reaction of the acenaphthylene dianion with methanol followed by methyl iodide:
According to the procedure described above, acenaphthylene (0.761 g, 5 mmol) was converted into the dianion and allowed to react with methanol (0.146 ml, 5 mmol) at -70°C. After stirring for 15 minutes at room temperature, the mixture was cooled again to -70°C; methyl iodide (0.311 ml, 5 mmol) was added and stirring was continued at room temperature for 30 minutes. The reaction was quenched with water. This resulted, after work-up, in the isolation of 1,5-dihydro-1-methylacenaphthylene in more than 95% yield.

1,5-Dihydro-1-methylacenaphthylene
^{1}H NMR ($CDCl_3$, TMS) δ 7.18-7.08 (m, 3H, H-6, H-7, H-8), 6.50 (dt, $J_{3,4}$ = 10.0, $J_{3,5}$ = 2.1, 1H, H-3), 5.95 (dt, $J_{4,3}$ = 10.0, $J_{4,5}$ = 3.8, 1H, H-4), 5.85 (d, $J_{1,2}$ = 1.9, 1H, H-2), 3.61-3.52 (m, 3H, H-1, H-5), 1.26 (d, $J_{Me,1}$ = 7.3, 3H, CH_3).

Rearrangement to 1-methylacenaphthene was achieved by stirring for two hours in acetone with a few drops of HCl. The conversion was complete and 1-methylacenaphthene was isolated after extraction with light petroleum (boiling range 40-60ºC), drying over $MgSO_4$ and concentration in >95% yield.

1-Methylacenaphthene
^{1}H NMR ($CDCl_3$, TMS) δ 7.57 (d, J = 8.2, 2H, H-5 and H-6), 7.45-7.39 (m, 2H, H-4 and H-7), 7.21 (d, $J_{7,8 = 3,4}$ = 6.9, 1H, H-3, H-8), 3.70 (m, 1H, H-1), 3.59 (dd, $J_{2,2}$ = 16.9, $J_{2,1}$ = 8.0, 1H, H-2_{trans}), 2.95 (d, $J_{2,2}$ = 16.9, $J_{2,1}$ = 3.2, 1H, H-2_{cis}), 1.45 (d, $J_{Me,1}$ = 6.9, CH_3).
^{13}C NMR ($CDCl_3$) δ 150.8 (C-2a or C-8a), 144.5 (C-2a or C-8a), 138.2 (C-8b), 131.4 (C-5a), 127.8 (C-4 and C-7), 122.4 (C-5 or C-6), 122.2 (C-5 or C-6), 119.1 (C3 or C8), 118.3 (C3 or C8), 39.7 (C2), 37.9 (C1), 21.7 (CH_3).

Generation of the acenaphthylene dianion in an NMR tube:
In a glove bag under an atmosphere of argon, acenaphthylene (ca. 0.1 g), THF-d_8 (0.75 ml) and sodium wire (ca. 2 cm) were transferred into an NMR tube. After three freeze-pump-thaw cycles, the NMR tube was sealed under vacuum. After three hours of ultrasonic vibration the formation of the dianion was complete.

Acenaphthylene dianion (**1**)
^{1}H NMR (THF-d_8, 20ºC) δ = 7.63 (2 H, H-4 and H-7), 7.08 (2 H, H-1 and H-2), 7.06 (2 H, H-3 and H-8), 5.93 (2 H, H-5 and H-6).
^{13}C NMR (THF-d_8, 20ºC) : δ = 149.2 (C-5a), 137.7 (C-8b), 126.7 (C-4 and C-7), 123.4 (C-2a and C-8a), 96.9 (C-3 and C-8), 85.9 (C-1 and C-2), 82.6 (C-5 and C-6).
^{13}C NMR (THF-d_8, -80ºC) : δ = 148.6 (C-5a), 137.0 (C-8b), 126.9 (C-4 and C-7), 122.9 (C-2a and C-8a), 96.1 (C-3 and C-8), 84.7 (C-1 and C-2), 83.4 (C-5 and C-6).

Generation of the 5-hydroacenaphthylene anion in an NMR tube:

The acenaphthylene dianion (1 mmol) was prepared in THF-d_8 (1 ml) according to the general procedure. At room temperature one equivalent of methanol was added and the solution was transferred to an NMR tube and sealed.

5-Hydroacenaphthylene anion (**8**)

^{1}H NMR (THF-d_8) : δ = 6.84 (d, $J_{7,8}$ = 7.8, 1H, H-8), 6.86-6.33(m, 2H, H-3 and H-7), 6.17 (m, 1H, H-2), 6.03 (d, $J_{6,7}$ = 6.4, 1H, H-6), 5.55 (d, $J_{1,2}$ = 2.1, 1H, H-1), 4.78 (m, 1H, H-4), 3.93 (m, 1H, H-5).

^{13}C NMR (THF-d_8) : δ = 130.3 (C-8b), 129.7 (C-5a), 128.2 (C-8a), 127.0 (C-3), 118.1 (C-7), 115.5 (C-8), 112.1 (C-2), 110.6 (C-4), 110.5 (C-6), 106.2 (C-2a), 90.7 (C-1), 32.1 (C-5).

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