4

Reactivity of the 5-hydroacenaphthylene anion towards electrophiles: single electron transfer *vs.* S_N2

4.1 Introduction

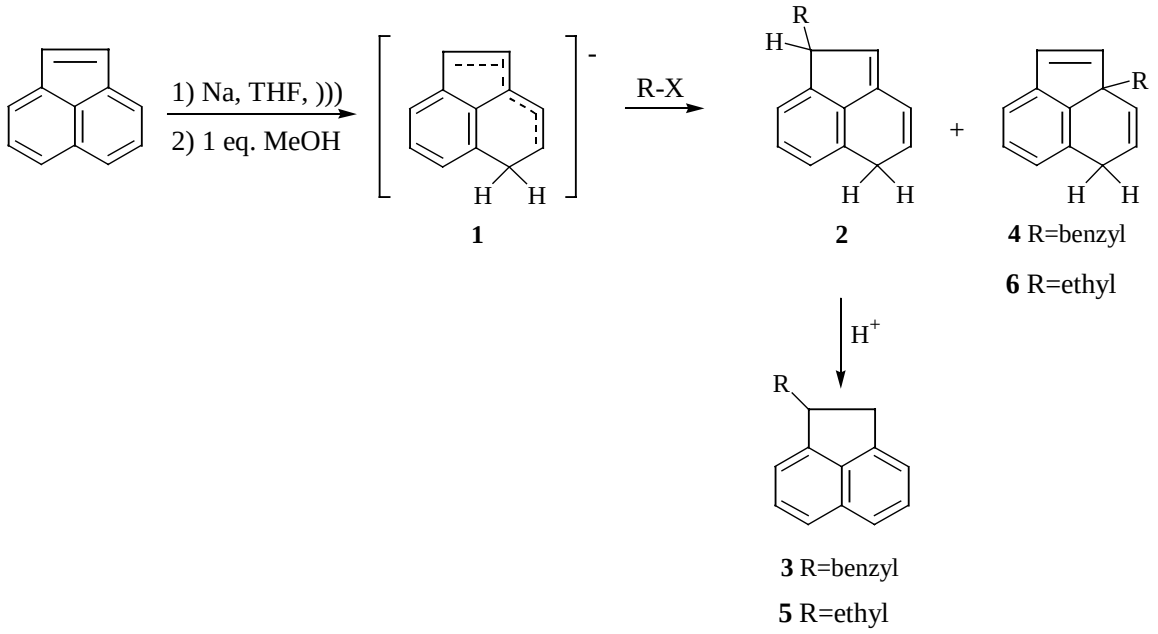
With alkyl halides such as methyl iodide and allyl bromide the 5-hydroacenaphthylene anion (**1**) reacts exclusively at position 1, resulting, after acidic work-up, in 1-substituted acenaphthenes (Chapters 2 and 3).[1,2] The next extension of the investigation of the reactivity of **1** involved the use of benzyl halides. From a synthetic organic point of view, coupling of the acenaphthene skeleton to a benzyl group would open the way to larger PAH: ring closure by means of irradiation[3,4,5] or metal-catalysed cyclodehydrogenation[6,7] might lead to e.g. cyclopenta[*def*]chrysene.

Preliminary results of the reaction of **1** with benzyl bromide as electrophile showed however that reaction took place not only at position 1 but also at position 2a.[2] The hardness or softness of the electrophile was presumed to be the cause of the different behaviour towards the 5-hydroacenaphthylene anion. In this chapter we study the reaction of the 5-hydroacenaphthylene anion with various benzyl halides (iodide, bromide, chloride and also tosylate) and for comparison also with ethyl halides (iodide, bromide and also tosylate) in order to obtain more evidence about the reaction mechanism. The results of these experiments required further mechanistic investigations. These include the use of sterically hindered electrophiles (isopropyl iodide and *tert*-butyl bromide), as well as the search for possible intermediates using *p*DNB (as electron scavenger) and radical scavengers (e.g., TEMPO). Furthermore, methods for the separation of the pure products have been developed.

4.2 Results

Acenaphthylene was converted into its 5-hydroanion (**1**) according to the procedure described earlier (Chapters 2 and 3).[1,2] The reaction mixture was cooled to -70ºC, one equivalent of benzyl bromide was added and the solution was stirred at room temperature during 30 minutes. Quenching with water and extraction with light petroleum (boiling range 40-60ºC) and the usual work-up, during which the initially formed 1-benzyl-1,5-dihydroacenaphthylene (**2**) rearranges to 1-benzylacenaphthene (**3**), gave **3** and 2a-benzyl-2a,5-dihydroacenaphthylene (**4**) as the major

products (more than 90% based on acenaphthylene) (Scheme 1). Acenaphthene and dibenzylated products were the only side products (less than 10%) observed.



***Scheme 1**: Reaction of the 5-hydroacenaphthylene anion with benzyl and ethyl halides (R = benzyl, ethyl, X = I, Br, Cl, OTs).*

Compounds **3** and **4** could not be separated by column chromatography over silica gel or silica gel impregnated with caffeine, by normal phase HPLC or by preparative gas chromatography. Therefore, the product mixture was treated with 3-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane, which led to the selective epoxidation of **4**. Subsequent removal of the oxidation product by means of silica gel column chromatography allowed the isolation of 1-benzylacenaphthene (**3**).

If the trisubstituted double bond, present in the initially formed 1-substituted product (**2**), is more reactive towards *m*CPBA than the double bonds in **4**, selective epoxidation of this bond would afford an isolation procedure for **4**. In order to avoid rearrangement of **2**, *m*CPBA was added to the reaction mixture before work-up. However, because of the competitive epoxidation of **4** it was not possible to obtain pure **4**. Eventually, 2a-benzyl-2a,5-dihydroacenaphthylene **4** was obtained pure by treatment of the product mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and removal of the 1-benzylacenaphthylene formed from **3** by subsequent column chromatography over silica impregnated with 10% caffeine.

The alkylation of the 5-hydroacenaphthylene anion **1** was also performed with benzyl chloride, benzyl iodide and benzyl tosylate, following the procedure as described for benzyl bromide. **3** and **4**

were obtained as major products. The ratios of **3** and **4** in these reactions, determined by NMR spectroscopy, are given in Table 1.

Treatment of **1** with one equivalent of ethyl iodide gave substitution at positions 1 and 2a in a 5:1 ratio (Table 1) and a mixture of 1-ethylacenaphthene **5** and 2a-ethyl-2a,5-dihydroacenaphthylene **6** was isolated. The use of one equivalent of ethyl bromide resulted in the formation of more 1-substituted product. However, use of the harder ethyl tosylate gave a 1:1 mixture of **5** and **6**. **5** could be isolated by the method described above. It was however not possible to oxidise **5** selectively by DDQ to obtain pure **6**.

Table 1*: Reaction of the 5-hydroacenaphthylene anion with benzyl and ethyl halides.*

Electrophile	ratio **3** : **4**	Electrophile	ratio **5** : **6**
Benzyl tosylate	1:0.6	Ethyl tosylate	1:1
Benzyl chloride	1:0.9	Ethyl chloride	N.D.
Benzyl bromide	1:1.2	Ethyl bromide	7:1
Benzyl iodide	1:1.0	Ethyl iodide	5:1

Reaction of **1** with one equivalent of isopropyl iodide gave a product mixture which contained, according to NMR, 30% acenaphthene, 35% 1-(2-propyl)acenaphthene and 35% 2a,5-dihydro-2a-(2-propyl)acenaphthene. Treatment of **1** with one equivalent of *tert*-butyl bromide gave only 20% substitution products, which contained *tert*-butyl groups at positions 1 and 2a in a 1:1 ratio, and almost 80% acenaphthene.

The reaction of **1** with benzyl bromide was also performed in the presence of the electron scavenger *para*-dinitrobenzene (*p*DNB) and radical scavengers (di-*tert*-butyl nitroxide and TEMPO), following the general procedure. The product ratios, which were determined with NMR, are given in Table 2. A similar experiment was performed with ethyl iodide in the presence of TEMPO (Table 2).

Table 2: *Effect of addition of electron or radical scavengers on the reaction of* ***1*** *with benzyl bromide and ethyl iodide.*

Electrophile	Additive	1-subst. prod. (%)	2a-subst. prod.(%)	acenaphthene (%)
Benzyl bromide	none	46	46	8
	0.5 eq. *p*DNB	24	24	48
	1 eq. di-*t*BuNO	33	33	32
	1 eq. TEMPO	24	24	51
Ethyl iodide	none	80	16	4
	1.5 eq. TEMPO	75	8	15

4.3 ^{1}H and ^{13}C NMR spectroscopy

The ^{1}H NMR spectrum of 1-benzylacenaphthene (**3**) consists of 11 aromatic and 5 benzylic protons. The aromatic part of the spectrum consists of two separate ABC patterns for the acenaphthene part and one A_2B_2C pattern for the phenyl group. In addition to the expected ortho- and meta-couplings in the naphthalene skeleton, H-3 and H-5 show small couplings with H-2 and H-2'. Similar couplings can be observed between H-6 and H-1 and between H-8 and H-1. These couplings were confirmed by H-H-COSY and decoupling experiments. The non-aromatic part shows an ABCDE pattern. The two protons at C-2, with a large negative geminal coupling constant, have different coupling constants with H-1, the cis-coupling being the larger one. H-1 also couples with the distinguishable protons at C-9 (see experimental section). This difference between H-9 and H-9' is induced by the chirality at C-1, but the assignment of the individual protons on the basis of a molecular model and these NMR results is not possible. Selective substitution of H-9 or H-9' with deuterium is necessary to discriminate between both protons.[8,9] The ^{13}C NMR spectrum was consistent with the structure of **3**.

In the spectrum of 2a-benzyl-2a,5-dihydroacenaphthylene (**4**) 8 aromatic protons, 4 olefinic and 4 benzylic protons can be recognised. The aromatic part of the spectrum consists of an ABC pattern for H-6, H-7 and H-8 and one A_2B_2C pattern for the phenyl group. H-1 and H-2 appear in a doublet at relatively low field, as can be expected by comparison with the ^{1}H NMR spectrum of styrene. The other olefinic protons H-3 and H-4 give together with H-5 and H-5' an ABX_2 pattern. In the boat-shaped six-membered ring, H-5 (pseudo-equatorial) and H-5' (pseudo-axial) can be clearly distinguished (see experimental section) by their different couplings with H-3 and H-4, due to the different dihedral angles. The benzylic protons H-9 and H-9' have different chemical shifts induced by chirality, but cannot be assigned on the basis of the molecular structure of **4**. The ^{13}C NMR spectrum was consistent with the structure of **4**.

The spectra of **5** and **6** were similar to the spectra discussed above.

4.4 Discussion

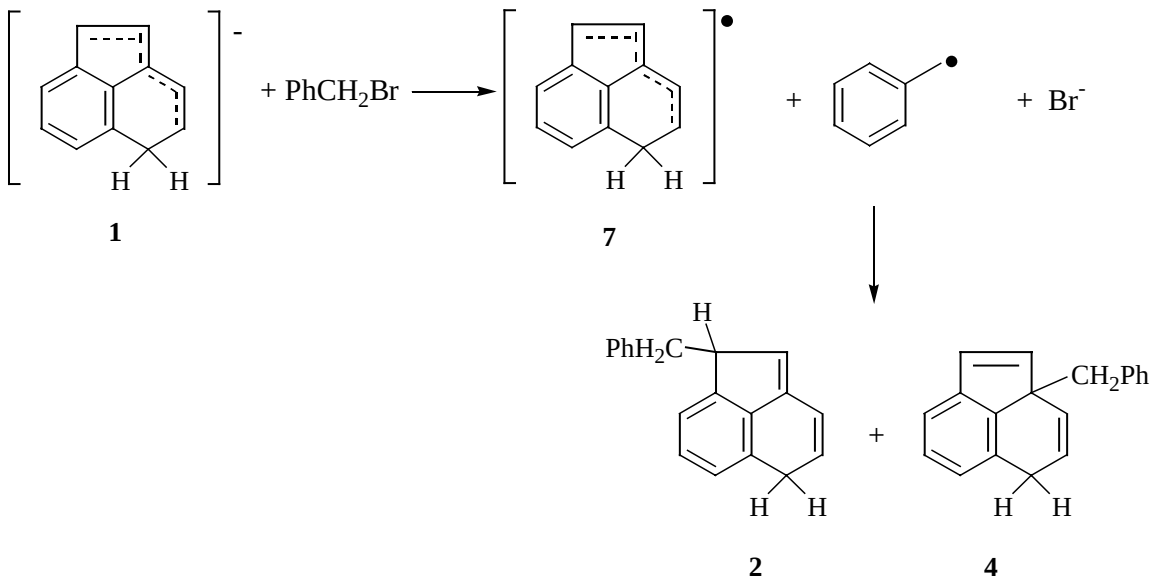
Reaction of the 5-hydroacenaphthylene anion **1** with alkyl halides such as methyl iodide and allyl bromide occurs at carbon atom 1. This may be due to the presence of the highest charge and a high HOMO coefficient at this carbon atom (Chapter 2).[1]

The charge distribution in **1** can be inferred from its ^{13}C NMR chemical shifts. From the order of these shifts (see Chapter 2, Table 2) C-1 appears to have the highest charge, in agreement with the calculations. A substantial amount of charge is also found at C-2a, less charge is present at C-4. In semiempirical (PM3)[2] and *ab initio* calculations (Chapter 2) the carbon atoms with the highest charge are C-1 (-0.21), C-4 (-0.17), C-6 (-0.16) and C-2a (-0.12). The highest HOMO coefficient is, however, found at C-2a (0.303), followed by C-1 (-0.275) and C-4 (-0.210).

In the reaction of benzyl bromide with **1** substitution takes place at position 1 as well as at 2a, in a ratio of 1:1. Such a change in regioselectivity with change in electrophile has been reported in the literature for the reaction of the 5-hydropyrenyl anion with soft electrophiles such as benzyl iodide and *n*-propyl iodide.[10,11] In this case the results were rationalised by the assumption that these electrophiles are soft and react at the position with the highest HOMO. In parallel, the hard-softness of electrophiles might be an important factor in determining at which position of **1** alkylation takes place. Therefore, **1** was treated with benzyl iodide, benzyl bromide, benzyl chloride and benzyl tosylate in order to investigate the influence of the nature of the leaving group.[12] Surprisingly, the leaving group did hardly affect the product distribution in the case of iodide, bromide and chloride (Table 1). The reaction of **1** was also performed with ethyl iodide, ethyl bromide and ethyl tosylate. Now, the hardest electrophile of the three, ethyl tosylate, gave the largest percentage of substitution at position 2a (Table 1). This is a strong indication that the hard-soft effect of the leaving group is not a major factor in determining the product distribution.

The following question now arises: which factors do determine the reactivity of the various positions in the hydroanion towards alkyl halides? If an S_N2 reaction would be possible at position 2a, thus creating a quaternary carbon atom, this must certainly be found for the small methyl iodide. But in the reaction of **1** with methyl iodide, absolutely no 2a-substituted product was observed. Bulkier electrophiles than methyl iodide do react at position 2a and this indicates that the reaction at 2a does not follow the S_N2 pathway. The mode of attack must be related to the nature of the interaction between nucleophile and electrophile.

In reactions with electron-rich nucleophiles, the single electron transfer (SET) mechanism can be competitive with the S_N2 mechanism. If **1** reacts via electron transfer, the 5-hydroacenaphthylene radical **7** will be an intermediate (Scheme 2).



***Scheme 2**: Reaction of the 5-hydroacenaphthylene anion with benzyl bromide via electron transfer.*

The recombination of the benzyl radical and **7** will take place at the positions with the highest spin densities (Figure 1), which are positions 1 and 2a according to *ab initio* calculations (ROHF/6-31G(d,p), restricted open shell, see Experimental section). The product ratio of **3** and **4** is 1:1, although carbon atom 1 has a lower spin density than carbon atom 2a. Positiion 1 is however more easily accessible for the electrophile. Apparently, the spin density at C-4 is not high enough to be able to compete with the other two carbon atoms.

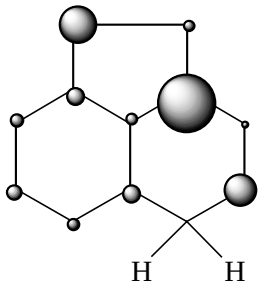


***Figure 1**: Total atomic spin densities in the 5-hydroacenaphthylene radical (**7**).*

The nature of the halide is one factor upon which the competition between S_N2 and SET in a substitution reaction with an alkyl halide depends. The transition states of both reactions will be influenced to a different degree by a change of leaving group.[13,14,15] The electron-acceptor ability (reduction potential) of the alkyl halide is an important factor in determining the possibility of SET and it increases in the order OTs <Cl<Br<I.[16,17,18,19] The order of reactivity observed in S_N2 reactions with primary alkyl halides is OTs>I>Br>Cl.[20] Therefore, reactions of alkyl tosylates are

more likely to proceed via an S_N2 mechanism whereas those of alkyl iodides will favourably proceed by SET.

In the case of simple alkyl halides, including benzyl halides, concerted electron transfer-bond breaking prevails, resulting in an alkyl radical and an halide ion.[21,22,23] Thus, the reactive intermediate after SET is identical for all leaving groups and reaction of this species will therefore result in the same substitution pattern for all leaving groups if SET is the exclusive mechanism.[24]

In the S_N2 mechanism primary alkyl halides will react more rapidly than more crowded derivatives. Decrease of reaction rate due to steric hindrance is less pronounced in the SET mechanism. To understand this inequality the transition states (TS) for both reaction pathways should be regarded.[25,25,26] Increase of steric hindrance in the transition state will result in bond loosening and will increase the TS barrier more for S_N2 than for SET.[27,28] In addition to steric factors, inhibition or hindering of the coupling process by electronic or geometric factors will result in a preference for the SET pathway.[25]

The benzyl group lowers the reduction potential with respect to simple alkyl groups and will therefore more easily undergo electron transfer.[29] More sterically hindered alkyl halides can also be more easily reduced and will therefore give more SET than their linear analogues. [18,30] This influence of the bulkiness of the reagent was confirmed by experiments with (aromatic radical anions and) a variety of alkyl halides.[14,15,17,31]

Applying this knowledge to the reaction of the 5-hydroacenaphthylene anion with benzyl halides demonstrates that the SET mechanism is consistent with the data. The product distribution is rather independent of the leaving group for iodide, bromide and chloride. This implies that the reaction pathway is the same for each halide and is in accordance with the assumption that in these cases SET is the principal reaction pathway. For benzyl tosylate the product distribution shifts towards more 1-substituted products. This may be due to the higher reactivity of tosylates in S_N2 reactions and their lower reactivity in SET reactions in relation to the other halides, because of their higher reduction potential. Ethyl iodide gives more 2a-substituted products than ethyl bromide but less than the benzyl halides. Ethyl halides have higher reduction potentials than the corresponding benzyl halides and will thus tend to give less SET products. Ethyl tosylate is an exception in its reactivity towards the hydroanion. However, it should be realised that the tosylate group is bulky and that the S_N2 reaction with the bulky hydroanion will therefore be seriously hindered.

To obtain further experimental evidence for the SET mechanism the following experiments were performed:

*1) Reaction of **1** with isopropyl iodide and tert-butyl bromide.*

These electrophiles were chosen because they are known to favour the electron transfer mechanism in their reaction with nucleophiles because of their steric proportions.[18,25,30] Isopropyl iodide gave substitution at both positions 1 and 2a, in a 1:1 ratio.
The reaction of the hydroanion with *tert*-butyl bromide gave, next to acenaphthene, circa 20% substitution products; the products formed were C-1 and C-2a substituted acenaphthenes in a 1:1 ratio. The reluctance of isopropyl iodide and *tert*-butyl bromide to undergo S_N2 reactions and the 1:1 ratio of the C-1 and C-2a substituted products validate the assumption that when exclusive SET reaction takes place substitution occurs to the same extent at positions 1 and 2a. Furthermore it should be noted that the bulkiness of the electrophile influences the reaction path (S_N2 *versus* SET), but does not affect the substitution ratios, which depend, in the case of SET, on the spin density distribution in **7**.

*2) Reaction of **1** with benzyl bromide in the presence of the electron scavenger para-dinitrobenzene.*
0.5 Equivalents of *para*-dinitrobenzene (*p*DNB) were added to the mixture of **1** and benzyl bromide in order to investigate if electron transfer is possible from the hydroanion to an electron scavenger.[20] In comparison with the reaction without electron scavenger, less benzylated products were found in the product mixture and more acenaphthene. From the decrease of the amount of substitution products we may conclude that electrons from the hydroanion were transferred to *p*DNB and thus that SET is possible. The resulting 5-hydroacenaphthylene radical is converted by hydrogen transfer into a dihydroacenaphthylene derivative, which rearranges to acenaphthene. The ratio of C-1 and C-2a benzylated products, determined by comparison of the characteristic NMR integrals, was unchanged. This indicates that either the two processes are delayed to the same extent or only electron transfer takes place.

*3) Reaction of **1** with alkyl halides in the presence of the radical scavengers di-tert-butyl nitroxide and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).*
An attractive possibility to discriminate between the S_N2 and SET mechanism is to investigate if free radical intermediates are present during the course of action. Because of the sensitivity of the reaction mixture to moisture and air it is difficult to perform the reaction in an EPR spectrometer. Therefore radical scavengers were used.[20,28]

Di-*tert*-butyl nitroxide (1 equivalent) was added to the reaction mixture of the hydroanion with benzyl bromide, following the general procedure. After the usual work-up the product mixture was analysed by NMR spectroscopy. The yield of substitution products was decreased, in favour of acenaphthene, but the **3** : **4** ratio did not change. The decrease of substitution products and the formation of acenaphthene indicates that radicals were present and thus that electron transfer has taken place. The yield of substitution products is lowered but not zero. Evidently the efficiency of the reaction with the radical scavenger is not so high that all the radicals are captured. The products

derived from the reaction of the radical scavenger with the benzyl radicals could not be isolated, due to the instability of the radical coupling products. The addition product of the radical scavenger to the 5-hydroacenaphthylene radical is probably converted into acenaphthene. If the S_N2 mechanism would be part of the reaction pathway, substitution at C-1 would not be hampered and thus the substitution ratio would have changed. The unchanged product ratio is a strong indication that the reaction of the hydroanion with benzyl bromide proceeds exclusively via SET.

Experiments were also performed with another radical scavenger: TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). Addition of TEMPO (1 equivalent) to the mixture of the 5-hydroacenaphthylene anion and benzyl bromide gave similar results as with di-*tert*-butyl nitroxide.

However, the use of TEMPO (1.5 equivalents) in the reaction of the 5-hydroacenaphthylene anion with ethyl iodide gave a change in the product distribution: **4** and **5** were now formed in the ratio 1 : 0.1 instead of 1 : 0.2. From the total amount of isolated product it could be concluded that the yield of **4** had not dramatically decreased. The decrease in yield of **5** leads to the conclusion that **5** must be formed in an SET reaction. Because the radical scavenger will not hinder S_N2 substitution, it is expected that the amount of product formed by S_N2 substitution will not be diminished. Therefore, the 1-substitution product in the reaction of the 5-hydroacenaphthylene anion with ethyl iodide is predominantly formed via an S_N2 mechanism.

These mechanistic investigations confirm the occurrence of electron transfer in the reaction of the 5-hydroacenaphthylene anion with electrophiles that are capable to accept electrons. In pure S_N2 reactions substitution takes place only at position 1 and in pure SET reactions substituents are found at positions 1 and 2a in a ratio of 1:1. The reaction of the 5-hydroacenaphthylene anion with ethyl iodide gives reaction products derived from both S_N2 and SET reactions. Alternatively, these results may be explained by assuming that the reaction type is intermediate between S_N2 and SET (continuum model).[13,14,24,32]

4.5 Conclusions

The reaction of the 5-hydroacenaphthylene anion **1** with electrophiles such as benzyl halides takes place at both positions 1 and 2a. 1-Benzylacenaphthene and 2a-benzyl-2a,5-dihydroacenaphthylene can be isolated by selective oxidation of the undesired isomer and subsequent separation by chromatography. The reactivity at position 2a cannot be ascribed to hardness-softness of the electrophile, but is more likely to be the result of electron transfer. The SET reaction takes place at position 1 as well as at 2a in a 1:1 ratio. After transfer of one electron, the 5-hydroacenaphthylene radical will react at the positions with the highest spin density. The observed product ratios from the reactions of electrophiles with **1** are in accordance with the electron affinities.

The use of electron scavengers (*p*DNB), radical scavengers (TEMPO) and more sterically hindered electrophiles corroborates the occurrence of the SET mechanism in the reaction of the 5-hydroacenaphthylene anion with electrophiles such as benzyl halides.

4.6 Experimental section

General: Acenaphthylene (Aldrich, 75%) was purified by treatment with DDQ and filtration over silica. Benzyl bromide, benzyl chloride, and ethyl tosylate were obtained from Acros and used without further purification but dried over molecular sieves (3Å, 8-12 mesh). Ethyl iodide was purchased from Acros and was extracted with a saturated sodium sulfite solution, predried over calcium chloride, distilled at atmospheric pressure and stored over molecular sieves (3Å, 8-12 mesh). Benzyl iodide was prepared from benzyl bromide by bromine-iodine exchange with potassium iodide in acetone. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3Å, 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. For the determination of the coupling constants we used the simulation program PERCH.[33]

General procedure:

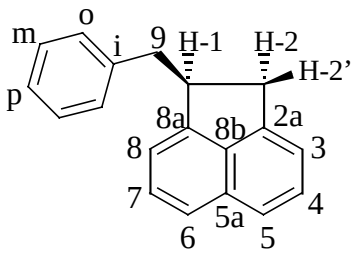
Into a dry 250 ml three-necked round-bottomed flask 125 ml of THF were distilled under an atmosphere of argon. Acenaphthylene (0.76 g,5 mmol) was added, together with freshly cut sodium (0.3 g, 13 mmol). Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon 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 0ºC, a deep green solution was obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70ºC and methanol (0.15 ml, 5 mmol) was added. The colour of the mixture turned red-brown. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. The mixture was cooled again to -70ºC and alkyl halide (5 mmol) was 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 40-60ºC), 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. Yields of substitution products are generally between 90 and 100%, 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. In the reaction with benzyl chloride 20 equivalents were used to accelerate the reaction.

Reaction of the acenaphthylene hydroanion with benzyl bromide:

To the 5-hydroacenaphthylene anion (5 mmol), prepared according to the general procedure, benzyl bromide (0.595 ml, 5 mmol) was added. Column chromatography over silica gel using light petroleum as eluent gave two fractions; the first consisted of acenaphthene (less than 10%) and benzyl bromide, the other contained the substitution products. Kugelrohr distillation gave a mixture of 1-benzylacenaphthene (**3**) and 2a-benzyl-2a,5-dihydroacenaphthylene (**4**). The residue contained a trace of at least two disubstituted products.

*Isolation of 1-benzylacenaphthene (**3**):*

To a mixture of **3** and **4** (ca. 5 mmol) in dichloromethane (25 ml) *m*-chloroperbenzoic acid (0.43 g, 2.5 mmol) was added and the reaction mixture was stirred overnight. Dichloromethane-water extraction, washing with Na_2SO_3-solution, followed by drying over $MgSO_4$ and evaporation of the solvent gave a mixture of **3** and (ep)oxidised **4**. Silica gel column chromatography with light petroleum gave 1-benzylacenaphthene as a light yellow oil. The oxidation products were not isolated and characterised. The yield of **3** varied between 40 and 50%, based on acenaphthylene.



1-Benzylacenaphthene (**3**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.61 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1H, H-5), 7.60 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6.8}$,1H, H-6), 7.43 (dd, $J_{3,4}$ = 6.7, $J_{4,5}$ = 8.2, 1H, H-4), 7.41 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.6, 1H, H-7), 7.23 (dddd, $J_{3,4}$ = 6.7, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1H, H-3), 7.20-7.12 (m, 5H, H-phenyl), 7.05 (ddd, $J_{7,8}$ = 6.6, $J_{1,8}$, $J_{6.8}$, 1H, H-8), 4.02 (dddddd, $J_{1,2}$ = 8.1, $J_{1,2'}$ = 2.3, $J_{9',1}$ = 8.9, $J_{9,1}$ = 7.5, $J_{1,8}$, $J_{1,6}$, 1H, H-1), 3.47 (dddd, $J_{2,2'}$ = -17.0, $J_{1,2}$ = 8.1, $J_{2.5}$, $J_{2,3}$, 1H, H-2), 3.19 (dd, $J_{9,9'}$ = -14.0, $J_{9,1}$ = 7.5, 1H, H-9), 3.10 (dddd, $J_{2,2'}$ = -17.0, $J_{1,2'}$ = 2.3, $J_{2',5}$, $J_{2',3}$, 1H, H-2'), 2.89 (dd, $J_{9,9'}$ = -17.0, $J_{9',1}$ = 8.9, 1H, H-9). $J_{1,6}$, $J_{6.8}$, $J_{1,8}$, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$ were observed but could not exactly be determined.

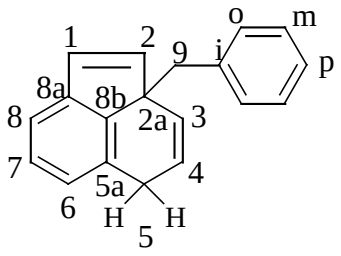
^{13}C NMR ($CDCl_3$) **:** δ = 148.5 (C-2a or C-8a), 144.1 (C-2a or C-8a), 140.3 (C-8b), 131.5(C-5a), 130.5 (C-ipso), 129.1 (2C-meta), 128.3 (2C-ortho), 127.8 (C-4 or C-7), 127.6 (C-4 or C-7), 126.1 (C-para), 122.8 (C-6), 122.3 (C-5), 119.2 (C-3 or C-8), 119.1 (C-3 or C-8), 44.5 (C-1), 42.6 (C-9), 37.3 (C-2).

$C_{19}H_{16}$: calcd. 244.1252; found 244.1276. MS; *m/z* (%): 244 (13), 165 (7), 154 (12), 153 (100), 91 (29), 65 (11).

*Isolation of 2a-benzyl-2a,5-dihydroacenaphthylene (**4**):*

To a mixture of **3** and **4** (ca. 5 mmol) in toluene 0.5 equivalent DDQ was added and the reaction mixture was stirred for 36 hours at room temperature. Filtration over hyflo, washing with a saturated sodium sulfite solution, drying over $MgSO_4$ and concentration was followed by chromatography

over silica impregnated with 10% caffeine. The first fraction, detected by an iodine bath, contained pure **4**. The oxidation products were not isolated and characterised.



2a-Benzyl-2a,5-dihydroacenaphthylene (**4**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ 7.19 (dd, $J_{7,8}$ = 7.3, $J_{6,7}$ = 7.6,1H, H-7), 7.18 (d, $J_{o,m}$ = 5.0, 2 H, H-o), 7.18 (d, $J_{p,m}$ = 5.0, 1 H, H-p), 7.16 (dd, $J_{7,8}$ = 7.3, $J_{6.8}$, 1H, H-8), 6.98 (dd, $J_{6,7}$ = 7.6, $J_{6,8}$, 1H, H-6), 6.97 (dd, $J_{o,m}$ = $J_{m,p}$ = 5.0, 2 H, H-m), 6.67 (d, $J_{1,2}$ = 5.5, 1H, H-1), 6.59 (d, $J_{1,2}$ = 5.5, 1H, H-2), 6.19 (ddd, $J_{3,4}$ = 9.2, $J_{3,5}$, $J_{3,5'}$ = 3.1, 1H, H-3), 6.14 (ddd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 5.5, $J_{4,5'}$ = 1.8, 1H, H-4), 3.12 (ddd, $J_{5,5'}$ = -19.6, $J_{3,5}$, $J_{4,5}$ = 5.5, 1H, H-5), 3.02 (ddd, $J_{5,5'}$ = -19.6, $J_{3,5'}$ = 3.1, $J_{4,5'}$ = 1.8, 1H, H-5'), 2.89 (d, $J_{9,9'}$ = -12.7, 1H, H-9), 2.62 (d, $J_{9,9'}$ = -12.7, 1H, H-9'), $J_{6.8}$ and $J_{3,5}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$)**:** δ = 148.7, 140.7, 138.2, 133.6 (C-8b, C-8a, C-5a, C-ipso), 142.5 (C-2), 130.4 (2 C-meta), 130.1 (C-1), 129.5 (C-4), 128.7 (C-3), 127.4 (2 C-ortho), 127.0 (C-7), 126.1 (C-para), 123.1 (C-6), 119.2 (C-8), 56.5 (C-2a), 46.2 (C-9), 29.7 (C-5)

$C_{19}H_{16}$: calcd. 244.1252; found 244.1209. MS; *m/z* (%): 244 (12), 152 (100), 91 (58), 65 (30).

Reaction of the acenaphthylene hydroanion with ethyl iodide:

To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, ethyl iodide (0.25 ml, 0.47 g, 3 mmol) was added. The products could not be separated using column chromatography over silica gel. Acenaphthene could be removed by Kugelrohr distillation or by crystallisation from methanol, yielding a mixture of 1-ethylacenaphthene (**5**) and 2a-ethyl-2a,5-dihydroacenaphthylene (**6**) (90-100%).

*Isolation of 1-ethylacenaphthene (**5**):*

To a mixture of **5** and **6** (5 mmol) in dichloromethane (25 ml) was added *m*-chloroperbenzoic acid (0.43 g, 2.5 mmol) and the reaction mixture was stirred overnight. Dichloromethane-water extraction, washing with Na_2SO_3-solution, followed by drying over $MgSO_4$ and concentration gave a mixture of **5** and (ep)oxidised **6**. Silica gel column chromatography with light petroleum gave **5** as a light yellow oil. The oxidation products were not isolated and characterised. The yield of **5** varies between 40 and 50%, based on acenaphthylene.

1-Ethylacenaphthene (**5**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.58 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6.8}$,1H, H-6), 7.57 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1H, H-5), 7.43 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.7, 1H, H-7), 7.42 (dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 8.2, 1H, H-4), 7.23 (ddd, $J_{7,8}$ = 6.7, $J_{1,8}$, $J_{6.8}$, 1H, H-8), 7.23 (dddd, $J_{3,4}$ = 5.9, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1H, H-3), 3.57 (m, 1H, H-1), 3.53 (dddd, $J_{2,2'}$ = -17.7, $J_{1,2}$ = 8.3, $J_{2.5}$, $J_{2,3}$, 1H, H-2), 3.02 (dddd, $J_{2,2'}$ = -17.7, $J_{1,2'}$ = 2.7, $J_{2',5}$, $J_{2',3}$, 1H, H-2'), 1.94 (ddq, $J_{9,9'}$ = -16.0, $J_{9,1}$ = 4.8, $J_{9,10}$ = 7.5, 1H, H-9), 1.64 (ddq, $J_{9,9'}$ = -16.0, $J_{9',1}$ = 8.9, $J_{9',10}$ = 7.5, 1H, H-9'), 1.02 (dd, $J_{9,10}$ = $J_{9',10}$ = 7.5, 3 H's, H-10). $J_{1,6}$, $J_{6.8}$, $J_{1,8}$, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$ were observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) **:** δ = 149.4 (C-2a or C-8a), 144.8 (C-2a or C-8a), 138.4 (C-8b), 131.4 (C-5a), 127.7 (C-4 and C-7), 122.5 (C-5 or C-6), 122.2 (C-5 or C-6), 119.0 (C-3 or C-8), 118.7 (C-3 or C-8), 44.9 (C-1), 37.0 (C-2), 29.1 (C-9), 11.8 (C-10).

$C_{14}H_{14}$: calcd. 182.1095; found 182.1105. MS; *m/z* (%): 182 (26), 153 (100), 140 (6), 84 (8), 60 (6), 51 (10).

2a-Ethyl-2a,5-dihydroacenaphthylene (**6**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.32-7.23 (m, 2H, H-7 and H-8), 7.06 (m, 1H, H-6), 6.81 (d, $J_{1,2}$ = 5.5, 1H, H-1), 6.67 (d, $J_{1,2}$ = 5.5, 1H, H-2), 6.37 (ddd, $J_{3,4}$ = 9.2, $J_{3,5}$, $J_{3,5'}$ = 3.2, 1H, H-3), 6.16 (ddd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 5.8, $J_{4,5'}$ = 1.7, 1H, H-4), 3.50 (m, 1H, H-5), 3.25 (ddd, $J_{5,5'}$ = -19.5, $J_{4,5'}$ = 1.7, $J_{3,5'}$ = 3.2, 1H, H-5'), 1.49 (m, 1H, H-9), 1.37 (m, 1H, H-9'), 0.92 (dd, $J_{9,10}$ = $J_{9',10}$ = 7.4, 3H, H-10), $J_{3,5}$ was observed but could not exactly be determined.

^{13}C NMR ($CDCl_3$) **:** δ = 142.3 (C-2), 134.8 (C-3), 130.6 (C-1), 128.3 (C-4), 128.1 (C-7), 123.1 (C-6), 119.0 (C-8), 33.3 (C-9), 30.4 (C-5), 10.6 (C-10), the quaternary C's were not observed.

Mechanistic investigations:

*Reaction of **1** with isopropyl iodide:*

To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, isopropyl iodide (0.60 ml, 1.02 g, 6 mmol) was added. From the NMR data it was concluded that the reduction was complete (no acenaphthylene) and the oil consisted of acenaphthene (30%), 1-(2-propyl)acenaphthene (35%) and 2a,5-dihydro-2a-(2-propyl)acenaphthene (35%). The total yield was 94%.

*Reaction of **1** with and* tert-*butyl bromide:*

To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, *tert*-butyl bromide (0.70 ml, 0.82 g, 6 mmol) was added. From the NMR data it was concluded that the reduction was complete (no acenaphthylene) and the oil consisted of acenaphthene (80%), 1-(*tert*-butyl)acenaphthene (10%) and 2a,5-dihydro-2a-(*tert*-butyl)acenaphthene (10%). The total yield was 97%.

Reaction in the presence of para-*dinitrobenzene (*p*DNB):*

The 5-hydroacenaphthylene anion was prepared according to the general procedure. At -60°C 0.5 equivalents of pDNB and 1 equivalent of benzyl bromide were added simultaneously to the reaction mixture. Stirring was continued at room temperature for 60 minutes after which the reaction was quenched with water. The addition of light petroleum (40-60), 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. This oil was analysed by NMR spectroscopy and consisted of acenaphthene (50%), **2** (25%) and **3** (25%). The total yield was 96%.

Reaction in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, free radical):

The 5-hydroacenaphthylene anion was prepared according to the general procedure. At -60°C 1.5 equivalents of TEMPO and 1 equivalent of ethyl iodide were added simultaneously to the reaction mixture. Stirring was continued at room temperature for 60 minutes after which period the reaction was quenched with water. The addition of light petroleum (40-60), 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. This oil was analysed by NMR spectroscopy and consisted of acenaphthene (15%), **4** (77%) and **5** (8%). The total yield was 97%.

Computational details

The calculations were carried out with the GAUSSIAN 94 suites of programs.[34] The geometry of radical **7** was fully optimised without symmetry restriction at the ROHF (restricted open shells) level by using the 6-31G(d,p) basis set.

5-Hydroacenaphthylene radical (**7**)*:*

Total atomic spin densities: 1 (0.192), 2 (0.012), 2a (0.489), 3 (0.004), 4 (0.141), 5 (0.001), 5a (0.037), 6 (0.015), 7 (0.027), 8 (0.019), 8a (0.036), 8b (0.013).

4.7 References

1 M.E. Van Loo, J. Lugtenburg, J. Cornelisse *Polycyclic Aromatic Compounds* accepted for publication
2 M.E. Van Loo, J. Lugtenburg, J. Cornelisse *Eur. J. Org. Chem.* **1998**, 1907-1914
3 F.B. Mallory, C.W. Mallory *Org. Reactions* **1984**, *30*, 1-456
4 W.H. Laarhoven *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 185-204
5 E.V. Blackburn, T.J. Timmons *Quart. Rev. Chem. Soc.* **1969**, *23*, 482-503
6 P.G. Copeland, R.E. Dean, D. McNeil *J. Chem. Soc.* **1960**, 1687-1689
7 Y. Altman, D. Ginsburg *J. Chem. Soc.* **1959**, 466-468
8 T. Wabayashi, K. Watanabe *Tetrahedron Lett.* **1977**, 4595-4598
9 J. Kobayashi, U. Nagai *Tetrahedron Lett.* **1977**, 1803-1804
10 C. Schnieders, K. Müllen, W. Huber *Tetrahedron* **1984**, 1701-1711
11 R. Brandsma, C. Tintel, J. Lugtenburg, J. Cornelisse *Synth. Commun.* **1985**, 91-93
12 N. Isaacs *Physical Organic Chemistry* 2nd ed. Longman Scientific & Technical, England, **1995**, 267-271
13 K. Daasbjerg, T.B. Christensen *Acta Chem. Scand.* **1995**, *49*, 128-132
14 H.S. Sørensen, K. Daasbjerg *Acta Chem. Scand.* **1998**, *52*, 51-61
15 J.F. Garst *Acc. Chem. Res.* **1971**, *4*, 400-406
16 E.C. Ashby *Acc. Chem. Res.* **1988**, *21*, 414-421
17 E.C. Ashby, C.O. Welder *J. Org. Chem.* **1997**, *62*, 3542-3551
18 C.P. Andrieux, I. Gallardo, J.-M. Savéant, K.-B. Su *J. Am. Chem. Soc.* **1986**, *108*, 638-647
19 E.C. Ashby, T.N. Pham *Tetrahedron Lett.* **1987**, *28*, 3183-3186
20 E.C. Ashby, D. Coleman *J. Org. Chem.* **1987**, *52*, 4554-4565
21 J.-M. Savéant *Adv. Phys. Org. Chem.* **1990**, *26*, 1-130
22 C.P. Andrieux, A. Le Gorande, J.-M. Savéant *J. Am. Chem. Soc.* **1992**, *114*, 6892-6904
23 J.-M. Savéant *Acc. Chem. Res.* **1993**, *26*, 455-461
24 C.P. Andrieux, J.-M. Savéant *J. Am. Chem. Soc.* **1993**, *115*, 8044-8049
25 A. Pross *Acc. Chem. Res.* **1985**, *18*, 212-219
26 F.G. Bordwell, J.A. Harrelson, Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1052-1057
27 G.N. Sastry, S. Shaik *J. Am. Chem. Soc.* **1998**, *120*, 2131-2145
28 E.C. Ashby, J.N. Argyropoulos *J. Org. Chem.* **1985**, *50*, 3274-3283
29 J.-M. Savéant *Advances in Electron Transfer Chemistry*, **1994**, *4*, 53-116
30 J.-M. Savéant *J. Am. Chem. Soc.* **1992**, *114*, 10595-10602
31 F.G. Bordwell, C.A. Wilson *J. Am. Chem. Soc.* **1987**, *109*, 5470-5474
32 A.C. Reddy, D. Danovich, A. Ioffe, S. Shaik *J. Chem. Soc., Perkin Trans. 2* **1995**, 1525-1539
33 R. Laatikainen, M. Niemitz, U. Weber, J. Sundelin, T. Hassinen, J. Vepsaelaeinen *J. Magn. Reson.* **1996**, *120*, 1-10
34 Gaussian 94, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, J.A. Peterson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioşlowski, B. Stefanov, A. Nanayakhara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian Inc., Pittsburg, PA, **1995**