Reactivity of the 5-Hydroacenaphthylene Anion Towards Electrophiles, 2[+] Single Electron Transfer vs. S_N2 Reaction

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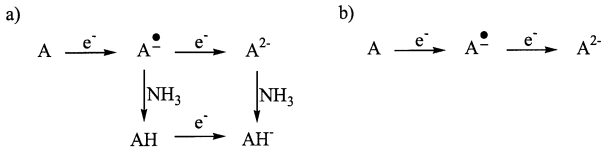
Reaction of the 5-hydroacenaphthylene anion with benzyl halides proceeds at carbon atom 1 as well as at carbon atom 2a, in the latter case creating a quaternary centre. The hardness-softness of the electrophiles was shown to play only a minor role in determining the regioselectivity of the reaction of the hydroanion with several benzyl and alkyl halides: the leaving group hardly affects the ratio of 1- and 2a-substituted products. This indicates that the alkylation might proceed by an electron transfer (SET) instead of an S_N2 mechanism. Further evidence for SET was obtained by the use of free radical and electron scavengers. The substitution products 1-benzylacenaphthene and 2a-benzyl-2a,5-dihydroacenaphthylene could be isolated and purified.

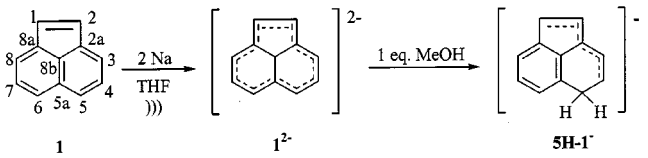
Introduction

An elegant method for the introduction of substituents in polycyclic aromatic hydrocarbons (PAHs) is reductive alkylation. In this reaction, anions of PAHs are treated with electrophiles such as alkyl halides. The advantages of this method are that relatively unreactive electrophiles can be used, and that the reactions often are regioselective. PAHs can be converted into their dianions by reaction with sodium in a mixture of liquid ammonia and THF. Under these conditions, however, hydroanions may be formed in addition to the PAH dianions, depending on the size and



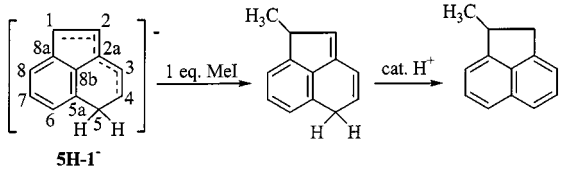
Scheme 1. Reduction schemes for polycyclic aromatic hydrocarbons, a: Birch-type, b: aprotic

the reactivity of the PAH (Scheme 1a,).[1][2][3] In a more convenient and more selective procedure than this Birch-like reduction, pure THF is used as solvent and the sodium is activated by ultrasonic vibration (Scheme 1, b). By means of this alternate procedure, acenaphthylene (**1**) can be converted easily and quantitatively into its dianion $\mathbf{1^{2-}}$ (Scheme 2).[4] The acenaphthylene dianion ($\mathbf{1^{2-}}$) can be protonated to form the 5-hydroacenaphthylene anion (**5H-1**$^-$) by addition of one equivalent of methanol to the reaction mixture (Scheme 2).[4]



Scheme 2. Selective synthesis of the 5-hydroacenaphthylene anion **5H-1**$^-$

With alkyl halides such as methyl iodide and allyl bromide, the 5-hydroacenaphthylene anion (**5H-1**$^-$) reacts exclusively at position 1, resulting in 1-substituted acenaphthenes (Scheme 3) after acidic workup.[4][5] However, preliminary results of this reaction using benzyl bromide as the electrophile showed that reaction took place not only at position 1, but also at position 2a.[5] The hardness or softness of the electrophiles was suspected to be the cause of their different behaviour towards the 5-hydroacenaphthylene anion (**5H-1**$^-$), a property which was also suggested for the reaction of the 1-hydropyrene anion.[6][7] In the present work we study the reactions of the 5-hydroacenaphthylene anion with various benzyl halides (iodide, bromide, chloride) and also with benzyl tosylate, and for comparison the corresponding reactions with ethyl halides (iodide, bromide) and tosylate, in order to obtain more information about the reaction mechanism. The results of these reactions required further mechanistic investigations, including 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.



Scheme 3. Reaction of the 5-hydroacenaphthylene anion (**5H-1**$^-$) with methyl iodide

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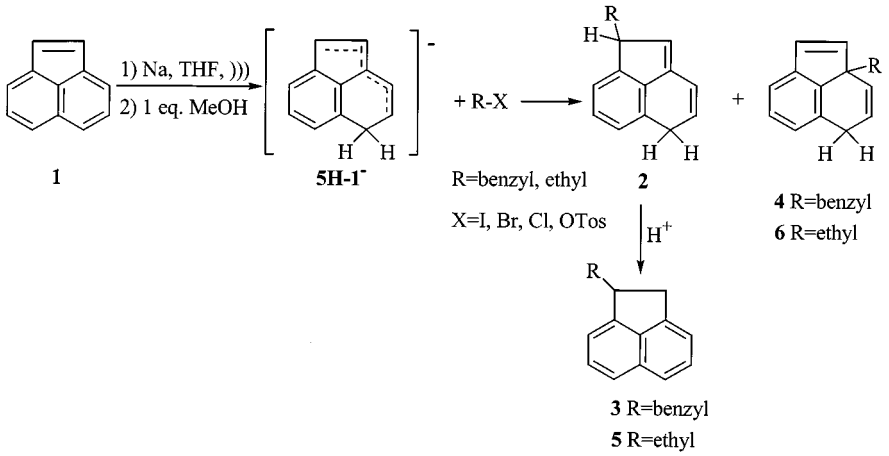


Scheme 4. Reaction of the 5-hydroacenaphthylene anion with benzyl and ethyl halides (R = benzyl, ethyl, X = I, Br, Cl, OTs)

Results

Acenaphthylene was converted into its 5-hydroanion (**5H-1**$^-$) according to the procedure described earlier.[4][5] The reaction mixture was cooled to –70 °C, one equivalent of benzyl bromide was added and the solution was stirred at room temperature during 30 minutes. Quenching with water and subsequent extraction with light petroleum (40–60 °C), followed by the usual workup, 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 4). Acenaphthene and dibenzylated products were the only side products observed. Pure **3** and **4** could be isolated by selective oxidation of the undesired isomer (See Experimental Section).

The alkylation of the 5-hydroacenaphthylene anion **5H-1**$^-$ was also performed with benzyl chloride, benzyl iodide, and benzyl tosylate, following the procedure as described for benzyl bromide. Compounds **3** and **4** were again obtained as major products. The ratios of **3** and **4** for these reactions, determined by NMR spectroscopy, are given in Table 1.

Table 1. Reaction of the 5-hydroacenaphthylene anion (**5H-1**$^-$) 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	-	-
Benzyl bromide	1:1.2	Ethyl bromide	7:1
Benzyl iodide	1:1.0	Ethyl iodide	5:1

Treatment of **5H-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**. Compound **5** could be isolated by the method mentioned above (See Experimental Section). It was not possible to obtain compound **6** in a pure form.

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

The reaction of **5H-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 by NMR, are given in Table 2. A similar experiment was performed with ethyl iodide in the presence of TEMPO (Table 2).

^{1}H and ^{13}C NMR Spectroscopy and Quantum Chemical Calculations

The 5-hydroacenaphthylene anion (**5H-1**$^-$) was prepared in [D_8]THF and transferred into an NMR tube. The measured spectra (^{1}H and ^{13}C) were similar to those recorded by Müllen and co-workers.[1] 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 ^{1}H and ^{13}C NMR spectra were assigned completely using H–H and C–H inverse COSY techniques. The ^{1}H 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 (For numbering see Scheme 2). Protons 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

Table 2. Effect of addition of electron or radical scavengers on the reaction of **5H-1**$^-$ with benzyl bromide and ethyl iodide

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

Table 3. Experimental and calculated ^{13}C NMR shifts (in ppm, given relative to the 25.3 ppm signal of THF and to TMS, respectively), Mulliken sum charges and HOMO coefficients of the 5-hydroacenaphthylene anion (**5H-1**$^-$)

Carbon atom	δ ^{13}C (exp.)	δ ^{13}C (calcd.)	Charge	HOMO
1	90.7	84.0	−0.21	−0.275
2	112.1	114.4	−0.10	+0.033
3	127.0	130.7	+0.03	−0.047
4	110.6	96.7	−0.17	−0.210
5	32.1	27.4	−0.02	+0.049
6	110.5	104.0	−0.16	−0.136
7	118.1	111.0	−0.09	+0.123
8	115.5	111.8	−0.09	+0.144
2a	106.2	93.0	−0.12	+0.303
5a	129.7	126.3	+0.03	−0.136
8a	128.2	124.9	+0.08	−0.115
8b	130.3	126.4	−0.11	+0.088

should be given to C-2a, which has a noteworthy upfield shift, indicating that a substantial amount of charge is also located at this carbon atom.

Although H-4 is found at relatively high field in the ^{1}H NMR (δ = 4.78), the ^{13}C NMR chemical shift indicates that much less charge is located at C-4 than at C-1. Because in ^{1}H NMR other factors such as ring current contribute to the shielding of hydrogens,[8] 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 is even positively charged. This is in accordance with the charge alternation concept as proposed by Rabinovitz and coworkers.[9]

In order to obtain additional information to help us understand the chemical reactions and the NMR spectra of the **5H-1**$^-$, quantum chemical calculations were performed. Ab initio methods were used to calculate the charge distribution, the HOMO coefficients, and the shielding constants for **5H-1**$^-$. The calculations were carried out with the GAUSSIAN 94 suite 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 ^{13}C NMR chemical shifts were calculated from the shielding factors and compared to the experimental data. The trend predicted by the calculations correlates very well with that observed (Table 3). 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 used as an indication of the most reactive positions.

Discussion

Reaction of the 5-hydroacenaphthylene anion **5H-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.[5]

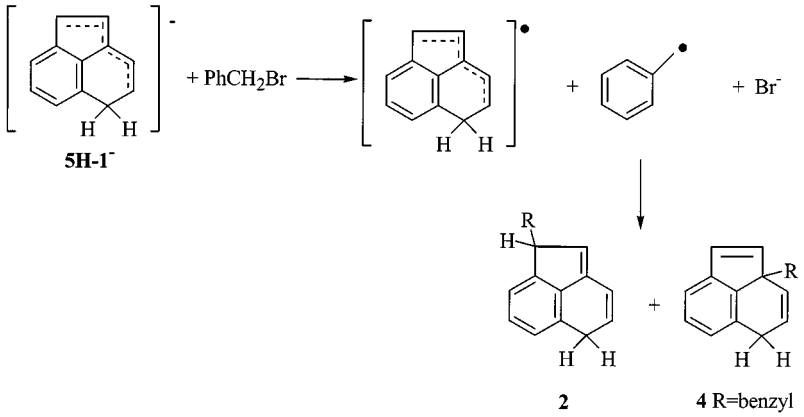
The charge distribution in anions of PAHs can be inferred from their ^{13}C NMR chemical shifts.[6] From the order of these shifts of **5H-1**$^-$ (Table 3), C-1 indeed appears to have the highest charge. A substantial amount of charge is also found at C-2a, and a smaller charge is present at C-4. In semiempirical (PM3)[5] and ab initio calculations, (Table 3) 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). The ab initio calculations predict the order of the chemical shifts very well (Table 3). Although C-2a has a very high HOMO coefficient, the reaction of **5H-1**$^-$ with methyl iodide indicates that no S_N2 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 with more difficulty 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 the interaction with the electrophile, and this might cause the low reactivity of C-4 towards electrophiles.

In the reaction of benzyl bromide with **5H-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-hydropyrene anion with soft electrophiles such as benzyl iodide and *n*-propyl iodide.[6][7] 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 hardness-softness of electrophiles might be an important factor in determining the position on **5H-1**$^-$ at which alkylation takes place. Therefore, **5H-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.[11] Surprisingly, the leaving group hardly affected the product distribution in the case of iodide, bromide, and chloride (Table 1). The reaction of **5H-1**$^-$ was also performed with ethyl iodide, ethyl bromide, and ethyl tosylate. Now, the hardest elec-

trophile 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 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 extent by a change of leaving group.[12][13][14] The electron-acceptor ability (reduction potential) of the alkyl halide is an important factor in determining the possibility of SET, and increases in the order OTs < Cl < Br < I.[15][16][17][18] For example, the reduction potential of benzyl bromide is –1.71, whereas that of benzyl chloride is –2.21 V (in DMF, vs. SCE at a glassy carbon electrode at 25 °C).[19][20] The order of reactivity observed in S_N2 reactions with primary alkyl halides is OTs>I>Br>Cl.[19] 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.



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

The question now 5is: which factors do determine the reactivity of the various positions in the hydroanion towards alkyl halides? If an S_N2 reaction was 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 **5H-1**$^-$ with methyl iodide absolutely no 2a-substituted products were 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.

The independence of the product distribution on the nature of the leaving group might be the result of an S_N1 type reaction. However, if the S_N1 reaction played a major role, the reactive electrophile would be a cation. The product would then be formed by combination of this cation with anion **5H-1**$^-$. The product distribution would then be expected to be determined predominantly by Coulomb interaction, and would thus depend strongly on the charge distribution of **5H-1**$^-$. Furthermore, the reaction of **5H-1**$^-$ with benzyl bromide and benzyl iodide proceeds almost instantaneously, which would not be the case for an S_N1 reaction, because in THF only a small fraction of the benzyl halide will be dissociated.

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

The recombination of the benzyl radical and **5H-1**$^\bullet$ 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]. The product ratio of **3** and **4** is 1:1, although carbon atom 1 has a lower spin density than carbon atom 2a. Position 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.

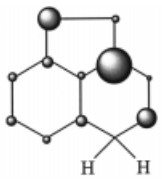


Figure 1. Spin densities in the 5-hydroacenaphthylene radical (**5H-1**$^\bullet$)

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.[22][23][24] 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.[25]

In the S_N2 mechanism, primary alkyl halides will react more rapidly than more crowded derivatives. A decrease in the 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.[26][27] Increasing steric hindrance in the transition state will result in bond loosening and will increase the TS barrier more for S_N2 than for SET.[28][29] 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.[26]

The benzyl group lowers the reduction potential with respect to simple alkyl groups and will therefore more easily undergo electron transfer.[20] More sterically hindered alkyl halides can also be more easily reduced and will therefore give more SET than their linear analogues.[17][21] This influence of the bulkiness of the reagent was confirmed by experiments of aromatic radical anions with a variety of alkyl halides.[13][14][16][30]

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 (because of their higher reduction potential) in relation to the other halides. 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 noted 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 **5H-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.[17][24][29] 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, besides 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 validates 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 case of SET, on the spin density distribution in **5H-1**$^\bullet$.

2) Reaction of **5H-1**$^-$ with benzyl bromide in the presence of the electron scavenger *para*-dinitrobenzene.

para-Dinitrobenzene (*p*DNB) was added to the mixture of **5H-1**$^-$ and benzyl bromide in order to investigate if electron transfer is possible from the hydroanion to an electron scavenger.[19] In comparison with the reaction without electron scavenger, less benzylated products were found in the product mixture and more acenaphthene (See Table 2). 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. Because *p*DNB is not known to hinder S_N2 reactions, it is likely that this reaction proceeds via SET only.

3) Reaction of **5H-1**$^-$ with alkyl halides in the presence of the radical scavengers di-*tert*-butyl nitroxide and 2,2,6,6-tetramethylpiperidinooxy (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 not possible to perform the reaction in an EPR spectrometer, therefore radical scavengers were used.[19][29]

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 workup the product mixture was analysed by NMR spectroscopy. The yield of substitution products decreased, in favour of acenaphthene, but the **3**:**4** ratio did not change (See Table 2). 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 was 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-tetramethylpiperidinooxy). 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 (See Table 2). 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: **5** and **6** were now formed in the ratio 1:0.1 instead of 1:0.2, and more acenaphthene was isolated. From the total amount of isolated product it could be concluded that the yield of **5** had not dramatically decreased. Compound **5** can be formed by S_N2 as well as by SET. Because the radical scavenger will not hinder the S_N2 substitution, the amount of product

formed by this reaction will the same. Product **6** can only be formed in the SET reaction. Because the SET reaction gives 1- and 2a-substitution products in a 1:1 ratio, it can be concluded from the diminishing amount of **6** that the reaction of **5H-1**$^-$ with ethyl iodide proceeds via both the S_N2 and the SET mechanism. The degree to which the reaction follows the SET reaction path is decreased by TEMPO from 33% to 18%.

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. It is likely that in pure S_N2 reactions, substitution takes place only at position 1 and in pure SET reactions substituents are found at both positions 1 and 2a in a ratio of 1:1. The reaction of the 5-hydroacenaphthylene anion with ethyl iodide (and also possible ethyl bromide) gives reaction products derived from both S_N2 (two thirds) and SET (one third) reactions.

Conclusions

The reaction of the 5-hydroacenaphthylene anion **5H-1**$^-$ with electrophiles such as benzyl halides takes place at both positions 1 and 2a. Selective oxidation of the undesired isomer and subsequent separation by chromatography allows for the isolation of both 1-benzylacenaphthene and 2a-benzyl-2a,5-dihydroacenaphthylene. 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 **5H-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.

Experimental Section

General: Acenaphthylene (Aldrich, 75%) was purified by oxidation 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 methoxide (generated in situ) 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.[32]

General Procedure: THF (125 mL) was distilled into a dry 250 mL three-necked round-bottomed flask under an atmosphere of argon. Acenaphthylene (0.761 g, 5 mmol) was added, together with 0.3 g (13 mmol) of freshly cut sodium. Directly after the addition, the flask was evacuated and sonicated for a period of 40 seconds. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After five hours of sonication, during which the temperature was kept at 0 °C, a deep green solution was obtained. The flask was then cooled in an ethanol-nitrogen bath to –70 °C and 0.146 mL (5 mmol) of methanol was added. The colour of the mixture turned red. The mixture was allowed to warm to room temperature and stirred for a further 10 minutes. The mixture was again cooled to –70 °C and 5 mmol of alkyl halide were added. Stirring was continued at room temperature for 30 minutes, after which the reaction was quenched with water. The addition of light petroleum (40–60 °C), 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 (**5H-1**$^-$) (5 mmol), prepared according to the general procedure, was added benzyl bromide (0.595 mL, 5 mmol). 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.

Separations of 3 and 4: 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 workup. 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 in a pure form 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.

Isolation of 1-Benzylacenaphthene (3): To a mixture of **3** and **4** (ca. 5 mmol) in dichloromethane (25 mL) was added *m*-chloroperben-

zoic 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 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** varies between 40 and 50%, based on acenaphthylene.

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 an A_2B_2C pattern for the phenyl group. In addition to the expected *ortho* and *meta* couplings, 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 nonaromatic 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. Proton H-1 also couples with the distinguishable protons at C-9 (see later in the Experimental Section). This difference between H-9 and H-9' is induced by the chirality at C-1 (Figure 2), but the assignment of the individual protons on the basis of a molecular model and the NMR results is not possible. Selective substitution of H-9 or H-9' with deuterium is necessary to discriminate between both protons.[33][34] The ^{13}C NMR spectrum was consistent with the structure of **3**.

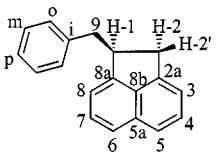


Figure 2. 1-Benzylacenaphthene

1-Benzylacenaphthene (3): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.61 (dddd, $J_{4,5}$ = 8.2 Hz, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.60 (ddd, $J_{6,7}$ = 8.2 Hz, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.43 (dd, $J_{3,4}$ = 6.7 Hz, $J_{4,5}$ = 8.2 Hz, 1 H, H-4), 7.41 (dd, $J_{6,7}$ = 8.2 Hz, $J_{7,8}$ = 6.6 Hz, 1 H, H-7), 7.23 (dddd, $J_{3,4}$ = 6.7 Hz, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1 H, H-3), 7.20–7.12 (m, 5 H, H-phenyl), 7.05 (ddd, $J_{7,8}$ = 6.6 Hz, $J_{1,8}$, $J_{6.8}$, 1 H, H-8), 4.02 (dddddd, $J_{1,2}$ = 8.1 Hz, $J_{1,2'}$ = 2.3 Hz, $J_{9',1}$ = 8.9 Hz, $J_{9,1}$ = 7.5 Hz, $J_{1,8}$, $J_{1,6}$, 1 H, H-1), 3.47 (dddd, $J_{2,2'}$ = –17.0 Hz, $J_{1,2}$ = 8.1 Hz, $J_{2.5}$, $J_{2,3}$, 1 H, H-2), 3.19 (dd, $J_{9,9'}$ = –14.0 Hz, $J_{9,1}$ = 7.5 Hz, 1 H, H-9), 3.10 (dddd, $J_{2,2'}$ = –17.0 Hz, $J_{1,2'}$ = 2.3 Hz, $J_{2',5}$, $J_{2',3}$, 1 H, H-2'), 2.89 (dd, $J_{9,9'}$ = –17.0 Hz, $J_{9',1}$ = 8.9 Hz, 1 H, H-9). $J_{1,6}$, $J_{6,8}$, $J_{1,8}$, $J_{2,5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, and $J_{2',3}$ were observed but could not be determined precisely. – ^{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 was added 0.5 equivalent DDQ 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.

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 an A_2B_2C pattern for the phenyl group. Protons H-1 and H-2 appear in a doublet at relatively low field, as can be expected on the basis of 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 later in the 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** (Figure 3).

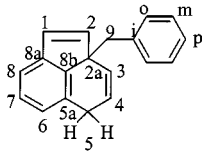


Figure 3. 2a-Benzyl-2a,5-dihydroacenaphthylene

2a-Benzyl-2a,5-dihydroacenaphthylene (4): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.19 (dd, $J_{7,8}$ = 7.3 Hz, $J_{6,7}$ = 7.6 Hz, 1 H, H-7), 7.18 (d, $J_{o,m}$ = 5.0 Hz, 2 H, H-o), 7.18 (d, $J_{p,m}$ = 5.0 Hz, 1 H, H-p), 7.16 (dd, $J_{7,8}$ = 7.3 Hz, $J_{6,8}$, 1 H, H-8), 6.98 (dd, $J_{6,7}$ = 7.6 Hz, $J_{6,8}$, 1 H, H-6), 6.97 (dd, $J_{o,m}$ = $J_{m,p}$ = 5.0 Hz, 2 H, H-m), 6.67 (d, $J_{1,2}$ = 5.5 Hz, 1 H, H-1), 6.59 (d, $J_{1,2}$ = 5.5 Hz, 1 H, H-2), 6.19 (ddd, $J_{3,4}$ = 9.2 Hz, $J_{3,5}$, $J_{3,5'}$ = 3.1 Hz, 1 H, H-3), 6.14 (ddd, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 5.5 Hz, $J_{4,5'}$ = 1.8 Hz, 1 H, H-4), 3.12 (ddd, $J_{5,5'}$ = –19.6 Hz, $J_{3,5}$, $J_{4,5}$ = 5.5 Hz, 1 H, H-5), 3.02 (ddd, $J_{5,5'}$ = –19.6 Hz, $J_{3,5'}$ = 3.1 Hz, $J_{4,5'}$ = 1.8 Hz, 1 H, H-5'), 2.89 (d, $J_{9,9'}$ = –12.7 Hz, 1 H, H-9), 2.62 (d, $J_{9,9'}$ = –12.7 Hz, 1 H, H-9'), $J_{6,8}$ and $J_{3,5}$ were observed but could not be determined precisely. – ^{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 (**5H-1**$^-$) (3 mmol), prepared according to the general procedure, was added ethyl iodide (0.25 mL, 0.47 g, 3 mmol). 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 subsequent 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) (numbering similar to 3): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.58 (ddd, $J_{6,7}$ = 8.2 Hz, $J_{1,6}$, $J_{6,8}$, 1 H, H-6), 7.57 (dddd, $J_{4,5}$ = 8.2 Hz, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1 H, H-5), 7.43 (dd, $J_{6,7}$ = 8.2 Hz, $J_{7,8}$ = 6.7 Hz, 1 H, H-7), 7.42 (dd, $J_{3,4}$ = 5.9 Hz, $J_{4,5}$ = 8.2 Hz, 1 H, H-4), 7.23 (ddd, $J_{7,8}$ = 6.7 Hz, $J_{1,8}$, $J_{6,8}$, 1 H, H-8), 7.23 (dddd, $J_{3,4}$ = 5.9 Hz, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1 H, H-3), 3.57 (m, 1 H, H-1), 3.53 (dddd, $J_{2,2'}$ = –17.7 Hz, $J_{1,2}$ = 8.3 Hz, $J_{2,5}$, $J_{2,3}$, 1 H, H-2), 3.02 (dddd, $J_{2,2'}$ = –17.7 Hz, $J_{1,2'}$ = 2.7 Hz, $J_{2',5}$, $J_{2',3}$, 1 H, H-2'), 1.94 (ddq, $J_{9,9'}$ = –16.0 Hz, $J_{9,1}$ = 4.8 Hz, $J_{9,10}$ = 7.5 Hz, 1 H, H-9), 1.64 (ddq, $J_{9,9'}$ = –16.0 Hz, $J_{9',1}$ = 8.9 Hz, $J_{9',10}$ = 7.5 Hz, 1 H, H-9'), 1.02 (dd, $J_{9,10}$ = $J_{9',10}$ = 7.5 Hz, 3 H's, H-10). $J_{1,6}$, $J_{6.8}$, $J_{1,8}$, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, and $J_{2',3}$ were observed but could not be determined precisely. – ^{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) (numbering similar to 4): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.32–7.23 (m, 2 H, H-7 and H-8), 7.06 (m, 1 H, H-6), 6.81 (d, $J_{1,2}$ = 5.5 Hz, 1 H, H-1), 6.67 (d, $J_{1,2}$ = 5.5 Hz, 1 H, H-2), 6.37 (ddd, $J_{3,4}$ = 9.2 Hz, $J_{3,5}$, $J_{3,5'}$ = 3.2 Hz, 1 H, H-3), 6.16 (ddd, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 5.8 Hz, $J_{4,5'}$ = 1.7 Hz, 1 H, H-4), 3.50 (m, 1 H, H-5), 3.25 (ddd, $J_{5,5'}$ = –19.5 Hz, $J_{4,5'}$ = 1.7 Hz, $J_{3,5'}$ = 3.2 Hz, 1 H, H-5'), 1.49 (m, 1 H, H-9), 1.37 (m, 1 H, H-9'), 0.92 (dd, $J_{9,10}$ = $J_{9',10}$ = 7.4 Hz, 3 H, H-10), $J_{3,5}$ was observed but could not be determined precisely. – ^{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.

Generation of the 5-Hydroacenaphthylene Anion (5H-1$^-$) in an NMR Tube: The acenaphthylene dianion was prepared in [D_8]THF 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 (5H-1–): ^{1}H NMR ([D_8]THF): δ = 6.84 (d, $J_{7,8}$ = 7.8 Hz, 1 H, H-8), 6.86–6.33(m, 2 H, H-3 and H-7), 6.17 (m, 1 H, H-2), 6.03 (d, $J_{6,7}$ = 6.4 Hz, 1 H, H-6), 5.55 (d, $J_{1,2}$ = 2.1 Hz, 1 H, H-1), 4.78 (m, 1 H, H-4), 3.93 (m, 1 H, H-5). – ^{13}C NMR ([D_8]THF): 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).

Mechanistic Investigations: Reaction of 5H-1$^-$ with Isopropyl Iodide and *tert*-Butyl Bromide: To the 5-hydroacenaphthylene anion (3 mmol), prepared according to the general procedure, was added isopropyl iodide (0.60 mL, 1.02 g, 6 mmol). From the NMR data it was concluded that the reduction was complete (no acenaphthylene) and the resulting oil consisted of acenaphthene (30%), 1-(2-propyl)acenaphthene (35%) and 2a,5-dihydro-2a-(2-propyl)acenaphthylene (35%). The total yield was 94%.

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

Reaction in the Presence of *p*-Dinitrobenzene (pDNB): The 5-hydroacenaphthylene anion (**5H-1**$^-$) was prepared according to the general procedure. At –60 °C *p*DNB (0.5 equivalents) 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 °C), 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-Tetramethylpiperidinooxy (TEMPO, free radical): The 5-hydroacenaphthylene anion (**5H-1**$^-$) was prepared according to the general procedure. At –60 °C TEMPO (1.5 equivalents) and 1 equivalent of ethyl iodide 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 °C), 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 suit of programs.[34] The geometries were fully optimised without symmetry restriction at the HF (5-hydroacenaphthylene anion) and ROHF (5-hydroacenaphthylene radical, restricted open shells) level by using the 6–31G(d,p) basis set, and characterised by frequency calculations.

5-Hydroacenaphthylene Anion (5H-1$^-$): Mulliken sum charges: 1 (–0.207), 2 (–0.099), 2a (–0.123), 3 (+0.028), 4 (–0.168), 5 (–0.016), 5a (+0.028), 6 (–0.159), 7 (–0.092), 8 (–0.092), 8a (+0.08), 8b (–0.109). – HOMO coefficients: 1 (–0.275), 2 (0.033), 2a (0.303), 3 (–0.047), 4 (–0.210), 5 (0.049), 5a (–0.136), 6 (–0.136), 7 (0.123), 8 (0.144), 8a (–0.115), 8b (0.088). – Chemical shift (relative to TMS): 1 (84.0), 2 (114.4), 2a (93.0), 3 (130.7), 4 (96.7), 5 (27.4), 5a (126.3), 6 (104.0), 7 (111.0), 8 (111.8), 8a (124.9), 8b (126.4).

5-Hydroacenaphthylene Radical (5H-1$^•$): 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).

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