Reactivity of the 5-Hydroacenaphthylene Anion towards Electrophiles

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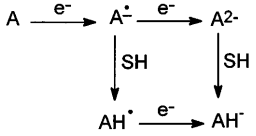
The dianion of acenaphthylene can be converted into the 5-hydroanion by protonation with one equivalent of methanol. Subsequent reaction with electrophiles such as allyl bromide and propargyl bromide occurs selectively at position 1, resulting in the formation of the novel 1-allylacenaphthene and 1-propargylacenaphthene. In addition to what was observed in the case of methyl iodide, the hitherto unknown 1,1-dialkylated acenaphthene derivatives are formed as minor products; probably the lower reactivity of the unsaturated bromides is responsible for this side reaction. From the products of the reactions with 3,3-dimethylallyl bromide and (bromomethyl)cyclopropane the mechanism was found to be S_N2. Reaction of the hydroanion with benzyl bromide takes place at position 1 as well as at position 2a. The reactivity of carbon 2a towards the soft electrophile benzyl bromide is attributed to the high HOMO coefficient at this position.

Introduction

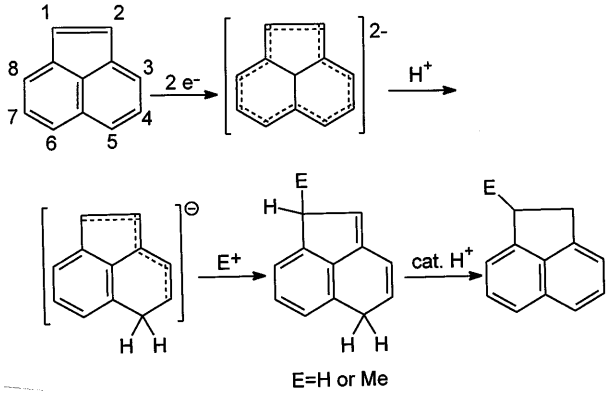
Polycyclic aromatic hydrocarbons (PAH) can be easily substituted by reductive alkylation. The advantage of reductive alkylation with respect to electrophilic aromatic substitution is that relatively unreactive electrophiles can be used. A second important advantage is that the reactions often are very selective. In the Birch-like reductive alkylation PAH are converted into their anions using sodium in a mixture of liquid ammonia and THF. Under these conditions the PAH can give dianions or hydroanions, depending on the size and reactivity of the PAH (Scheme 1).[1][2][3] A more convenient procedure is the preparation of the dianion in pure THF, using sodium and ultrasonic vibration.

Scheme 1. Reduction scheme for polycyclic aromatic hydrocarbons



The dianion of acenaphthylene is easily formed in spite of its small size.[4][5] It is known from the ^{13}C-NMR spectra of the dianion and from semiempirical calculations that the highest charge density is located at C-5.[6][7][8] The calculations show that the highest HOMO coefficient is also located on this carbon atom. Therefore, electrophiles are expected to react at position 5 of the acenaphthylene dianion. From experiments with proton donors it is known that the first equivalent of proton reacts selectively at position 5, resulting in the 5-hydroacenaphthylene anion (Scheme 2).[1] The next equivalent of protons is added at position 1, thus resulting in 1,5-dihydroacenaphthylene.[2][9]

Scheme 2. Reaction of the acenaphthylene dianion with electrophiles



Reaction of the hydroanion with one equivalent of methyl iodide results in the formation of 1-methyl-1,5-dihydroacenaphthylene in more than 90% yield.[10] Treatment with a few drops of HCl in acetone gives rearrangement to the more stable 1-methylacenaphthene.

In the present work we use the 5-hydroacenaphthylene anion in reactions with allyl bromide, 3,3-dimethylallyl bromide, propargyl bromide, and (bromomethyl)cyclopropane. This extension to allylic systems leads to introduction of functional groups at position 1 in acenaphthene and to the synthesis of seven novel compounds. Another reason for using these electrophiles is the possibility to study the mechanism of the reaction of the 5-hydroacenaphthylene anion with alkyl bromides.

Results

The 5-hydroacenaphthylene anion was prepared starting from acenaphthylene, which was converted into its dianion

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using 2.2 equivalents of sodium in anhydrous THF and ultrasonic vibration. Within 3−5 hours the colour of the solution turned deep green, indicating that the dianion had been formed. The reaction mixture was cooled to −70°C and exactly one equivalent of anhydrous methanol was added. The reaction mixture was stirred for a further 15 minutes at room temperature. After cooling the solution to −70°C one equivalent of allyl bromide was added to the hydroanion and the mixture was stirred at room temperature during a further 30 minutes. After extraction with light petroleum ether and the usual work-up, 1-allylacenaphthene (**1a**) was obtained as the major product. 1-Allyl-1,5-dihydroacenaphthylene, the initially formed product, is very unstable and rearranges easily to the acenaphthene derivative − not only under slightly acidic conditions, but also on a silica gel column or at elevated temperatures − and could not be isolated. GC-MS analyses of the crude product showed the presence of acenaphthene, a mono- and a diallylated acenaphthene in the ratio of 1:3:1 (Table 1). These products could not be separated by means of chromatography on a silica gel column. Kugelrohr distillation of the product mixture gave rise to polymerisation reactions. Therefore, preparative gas chromatography was used to separate the products and 50−100 mg of pure products were isolated for NMR measurements.

By means of NMR techniques the alkylation products were identified as 1-allylacenaphthene (**1a**) and 1,1-diallylacenaphthene (**1b**) (Scheme 3).

The same procedure was used with 3,3-dimethylallyl bromide as electrophile. 1-(3-Methyl-2-butenyl)acenaphthene (**2a**) and 1,1-bis(3-methyl-2-butenyl)acenaphthene (**2b**) were formed in a 3:1 ratio (Table 1). The products could easily be separated by preparative GC and were characterized by NMR.

Use of propargyl bromide gave similar results. The products, 1-propargylacenaphthene (**3a**) and 1,1-dipropargylacenaphthene (**3b**), were separated by preparative GC and could be isolated in a 3:1 ratio (Table 1).

With (bromomethyl)cyclopropane only the monoalkylated product was formed next to acenaphthene in a 1:2 ratio (Table 1). Separation was performed by crystallisation of the acenaphthene followed by Kugelrohr distillation of the resulting oil to yield 1-(cyclopropylmethyl)acenaphthene (**4**).

Table 1: Results of the reaction of the 5-hydroacenaphthylene anion with electrophiles[a]

Electrophile	overall yield	ratio A/1-R-A/1,1-R_2-A
Allyl bromide	96%	1:3:1
3,3-Dimethylallyl bromide	93%	1:3:1
Propargyl bromide	95%	1:3:1
(Bromomethyl)cyclopropane	96%	2:1:0

[a]A = acenaphthene, R = substituent.

The results of these reactions prompted us to also use benzyl bromide (see Discussion). Preliminary results showed that the reaction with benzyl bromide was less selective: alkylation occurred at position 1 as well as at position 2a.

^{1}H- and ^{13}C-NMR Spectroscopy

The ^{1}H- and ^{13}C-NMR spectra of the products were assigned using H-H and C-H inverse COSY techniques. The ^{1}H-NMR spectrum of 1-allylacenaphthene (**1a**) (Figure 1) consists of signals of 6 aromatic, 3 olefinic, 3 benzylic, and 2 allylic protons.

The aromatic part of the spectrum consists of two separated ABC patterns. Next to the expected *ortho* and *meta* couplings 3-H and 5-H show additional small couplings, which could be ascribed to coupling with 2-H and 2′-H. A similar coupling can be observed between 1-H and 6-H and between 1-H and 8-H. These couplings were confirmed by long-range H-H COSY and decoupling experiments. The non-aromatic part shows an ABCMNXYZ pattern. The two protons at C-2, with a large negative geminal coupling constant, have different coupling constants with 1-H, the *cis* coupling being the larger one. 1-H also couples with the distinguishable protons at C-9. This difference between 9-H and 9′-H 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 9-H or 9′-H with deuterium is necessary to discriminate between both protons.[11][12] The dddd′s from 9-H and 9′-H are due to the coupling with 10-H and allylic coupling with 11-H and 11′-H. 11-H and 11′-H have coupling constants of 16.8 and 10.3 Hz with 10-H, and can be assigned as (*E*) and (*Z*) respectively, because $J(Z) < J(E)$. For the determination of the coupling constants we used the simulation program PERCH. The ^{13}C-NMR spectrum was consistent with this structure.

The spectra of the other 1-substituted acenaphthenes were similar to the spectrum described above and all expected couplings were found. In the case of 1-(3-methyl-2-butenyl)acenaphthene (**2a**) the methyl groups showed allylic couplings with the olefinic proton. The aliphatic part in the spectrum of 1-(cyclopropylmethyl)acenaphthene (**4**) was too complex to obtain all the coupling constants.

In the 1,1-disubstituted acenaphthenes the molecules have a plane of symmetry. Therefore, both 2-H's are identical. The same might be expected for 9-H and 9′-H, but although the signals moved towards each other and the coupling between them decreased, they were still separated. This might be the result of steric interactions.

In 1,1-dipropargylacenaphthene a remarkable shift of the 8-H signal towards lower field is observed. This is probably caused by the influence of the π-electrons of propargyl substituents at C-1. A second deviation from the other spectra are the coupling constants between 6-H and both 7-H and 8-H. $J_{6,8}$ increased to 7.0 Hz, $J_{6,7}$ however decreased to 2.0 Hz.

The spectrum of 1-benzylacenaphthene (**5a**) and 2a-benzyl-2a,5-dihydroacenaphthylene (**5b**) was resolved using the H-H and C-H inverse COSY spectrum. The olefinic part of the spectrum confirmed the structure of 2a-benzyl-2a,5-dihydroacenaphthylene (**5b**). Because the products

Scheme 3. Reductive alkylation of acenaphthylene with alkyl bromides

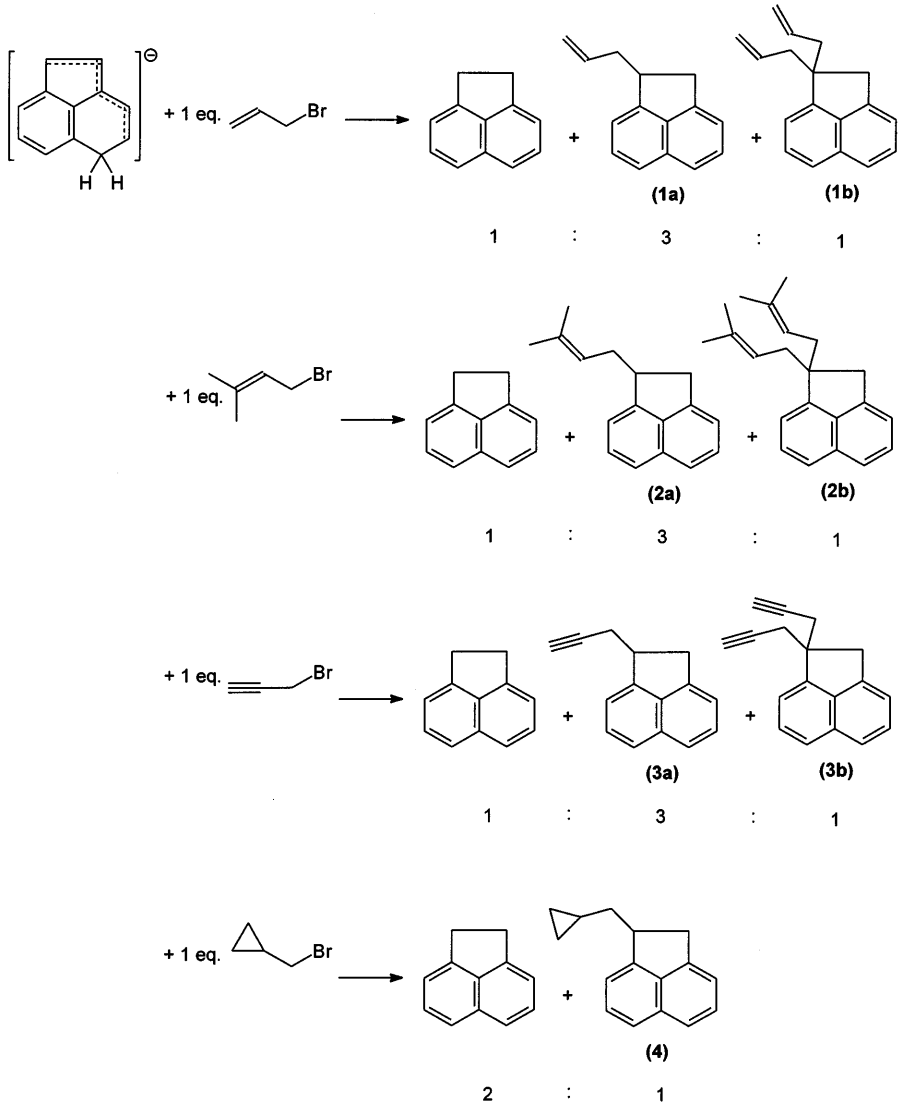
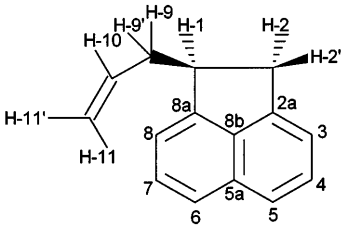


Figure 1. 1-Allylacenaphthene



could not be separated, it was impossible to assign the ^{13}C-NMR spectrum completely.

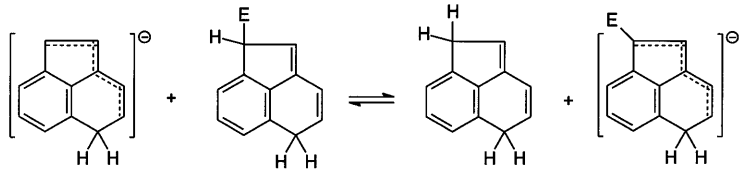
Discussion

The 5-hydroacenaphthylene anion can easily be prepared by addition of one equivalent of methanol to the dianion. This hydroanion reacts with methyl iodide at position 1 to give 1-methyl-1,5-dihydroacenaphthylene as the sole product. This unstable product rearranges under slightly acidic conditions to 1-methylacenaphthene. Allyl bromide is expected to react in the same way with the 5-hydroacenaphthylene anion, thus giving 1-allylacenaphthene. In our experiments three products were formed: acenaphthene and 1,1-diallylacenaphthene (**1b**) were isolated next to the expected 1-allylacenaphthene (**1a**). Obviously, the proton at position 1 of 1-allyl-1,5-dihydroacenaphthylene can easily be abstracted to give a 1-substituted 5-hydroanion. This hydroanion can react with a second allyl bromide to give the doubly substituted product. Two bases are present in the reaction mixture: one equivalent of methoxide, generated by the reaction of methanol with the dianion, and unreacted 5-hydroacenaphthylene anion. If the latter acts as a base this results in the formation of acenaphthene. Addition of two equivalents of allyl bromide gave approximately the same product ratio as in the experiment using only one equivalent of allyl bromide. If methoxide would be the most important base, a substantially larger amount of 1,1-diallylacenaphthene (**1b**) should be formed and less acenaphthene. Because the product ratio did not change, it may be concluded that the hydroanion is the strongest base in this process

(Scheme 4). Addition of potassium *tert*-butoxide, after addition of two equivalents of allyl bromide, did not result in more dialkylated product. Similarly, when a solution of 1,5-dihydroacenaphthylene was first treated with one equivalent of sodium methoxide and subsequently with excess electrophilic reagent, no substitution product could be detected. This also confirms the assumption that the 5-hydroacenaphthylene anion is a stronger base than methoxide. Apparently the 1-propynyl anion is a stronger base than 5-hydroacenaphthylene anion, because otherwise the reaction with propargyl bromide would yield much more acenaphthene, since the acetylenic moiety would be a proton donor for the 5-hydroacenaphthylene anion. The acidity of 1,5-dihydroacenaphthylene is expected to be in the vicinity of that of indene ($pK_a = 20$). The results of the reaction are in agreement with this estimated pK_a compared with the acidity of methanol ($pK_a = 15.2$) and acetylene ($pK_a = 25$).

In the reaction with methyl iodide no doubly alkylated product is formed. A possible explanation is that methyl iodide is more reactive towards the hydroanion, thus converting all the hydroanion immediately to the neutral compound and quenching further reaction. The higher reactivity of methyl iodide is in agreement with the influence of the leaving group (iodide vs. bromide) and the substituent (methyl vs. allyl).[13][14]

Scheme 4. Equilibrium in the reaction of the 5-hydroacenaphthylene anion with allyl bromide



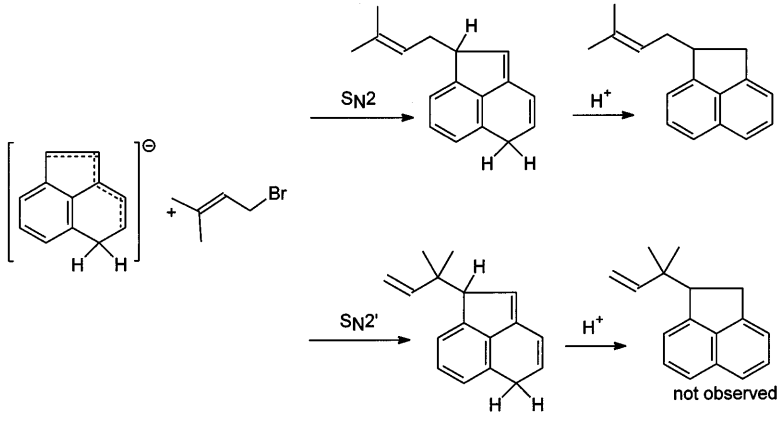
E=allyl

Allyl bromide can react by three mechanisms with nucleophiles: S_N2, S_N2', or single electron transfer (SET). From the results of the reaction of the hydroanion with 3,3-dimethylallyl bromide it can be concluded that the S_N2' mechanism does not play a significant role (Scheme 5). In the SET mechanism one electron is transferred from the hydroanion to the allyl bromide. The latter radical anion splits into an allyl radical and a bromide ion. The allyl radical will react at C-1 and at C-3, differently substituted in 3,3-dimethylallyl bromide. However, occurrence of the SET mechanism is unlikely because of the absence of products with methyl groups at C-9 (S_N2' product). The reaction products indicate that the S_N2 mechanism must be the most important one.

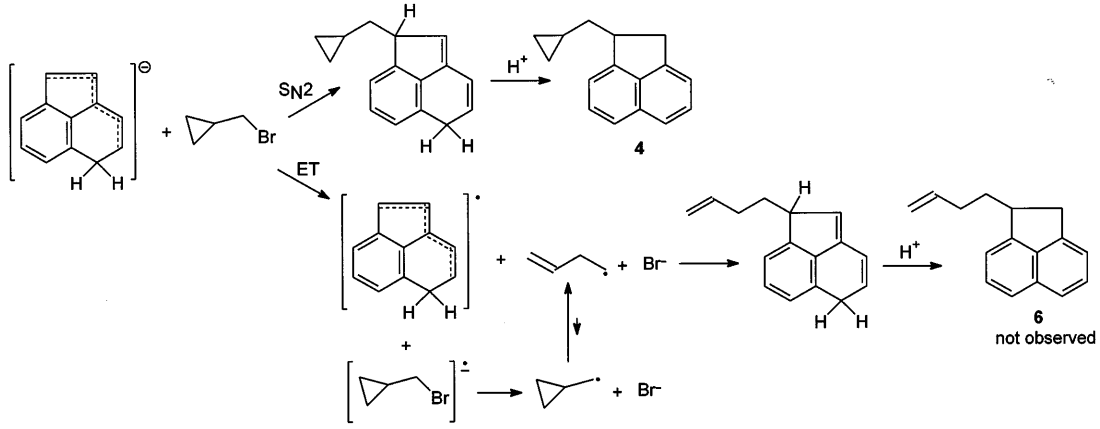
A similar conclusion can be drawn from the experiment with (bromomethyl)cyclopropane: if electron transfer were part of the substitution, the cyclopropylmethyl radical would be opened immediately to a butenyl radical (Scheme 6). 1-(3-Butenyl)acenaphthene (**6**) was, however, not observed. The yield of 1-(cyclopropylmethyl)acenaphthene (**4**) was relatively low (30%) in comparison with methyl iodide. This may be explained by the lower reactivity of (bromomethyl)cyclopropane compared to methyl iodide.

The reactivity at position 1 can be rationalised by the distribution of charge and the HOMO coefficients in the 5-hydroacenaphthylene anion (Figure 2). The calculations were performed with MOPAC93, using the PM3 method. The calculated charge distribution can be compared to the one inferred from the ^{13}C-NMR spectrum of the 5-hydroacenaphthylene anion. From the value of the chemical shift the highest charge is expected at carbon atom 1. To obtain the charge distribution, electrostatic potential calculation was used. This calculation, however, predicts a very high charge at C-4, which disagrees with the ^{13}C-NMR spectrum. Calculation of the total atomic charges did not lead to better agreement. Because reaction with alkyl halides normally occurs at carbon atom 1, we may assume that the highest charge is at C-1 indeed. The combination of highest charge and high HOMO coefficient is the reason that the reaction with most electrophiles takes preferably place at position 1. However, the highest HOMO coefficient is

Scheme 5. S_N2 and S_N2' mechanism of the reaction of 3,3-dimethylallyl bromide with the 5-hydroacenaphthylene anion

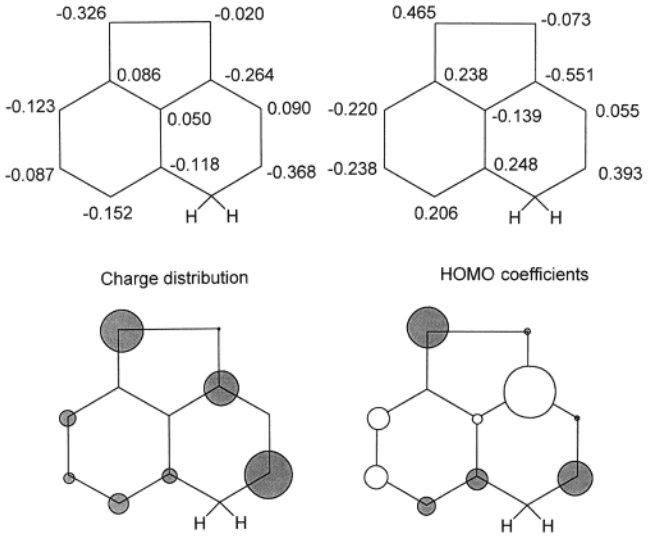


Scheme 6. Possible pathways for the reaction of (bromomethyl)cyclopropane with 5-hydroacenaphthylene anion



found at C-2a. It is known that soft electrophiles such as benzyl bromide will react at the position with the highest HOMO coefficient.

Figure 2. Distribution of charge and HOMO coefficients in 5-hydroacenaphthylene anion



Preliminary results of the reaction of benzyl bromide with 5-hydroacenaphthylene anion indicated that substitution occurred at position 1 as well as at 2a, in a ratio of 1:1 (Scheme 7). Similar results have been reported in the literature[15][16] for the reactions of the phenalenyl and hydropyrenyl anions with soft electrophiles such as benzyl iodide and propyl iodide. Here also the electrophiles reacted at the position with the highest HOMO, creating a quaternary carbon atom. Reactions of the 5-hydroacenaphthylene anion with electrophiles are subject to kinetic control, i.e. they are irreversible. We therefore assume that not the thermodynamic stability of the products but the hardness or softness of the electrophiles and the carbon atoms of the anion are responsible for the observed regioselectivity. Reactions with other soft electrophiles are still under investigation.

Conclusions

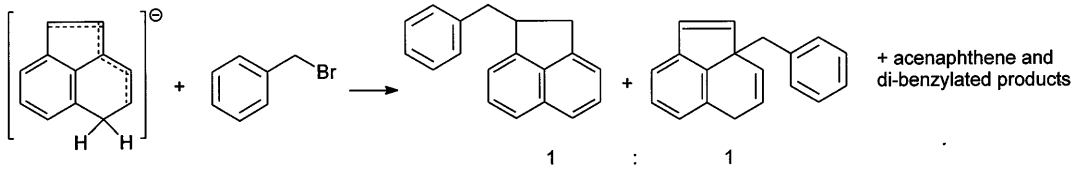
Reaction of the 5-hydroacenaphthylene anion with unsaturated alkyl bromides provides an easy route to introduce functional groups at position 1. In the case of allyl bromide, 3,3-dimethylallyl bromide and propargyl bromide a considerable amount of 1,1-dialkylated product could be isolated. This is the first route to obtain these disubstituted products selectively. The mechanism was proved to be S_N2 by reaction with dimethylallyl bromide and (bromomethyl)cyclopropane. Reaction with benzyl bromide is less selective because the soft electrophile reacts also at the position with the highest HOMO coefficient and a unique 2a-benzylated acenaphthylene is generated.

The authors wish to thank *Joke van Dijk-Knepper* for the preparative gas chromatography.

Experimental Section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration through silica gel. Allyl bromide, 3,3-dimethylallyl bromide, propargyl bromide, (bromomethyl)cyclopropane, and benzyl bromide were obtained from Acros and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3 Å, 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 with a Bruker WM-300 spectrometer. The 600-MHz ^{1}H-NMR spectrum of 1-propargylacenaphthene was recorded with a Bruker AM-600 spectrometer. All chemical shift

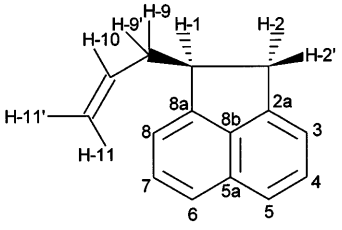
Scheme 7. Reaction of the 5-hydroacenaphthylene anion with benzyl bromide



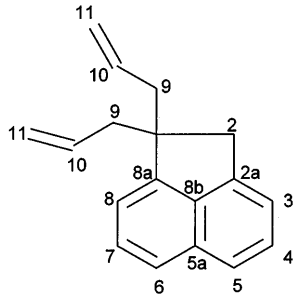
data (δ) are given in ppm relative to tetramethylsilane (TMS); the coupling constants (*J*) are given in Hz. Coupling constants in the range 1.2−0.5 Hz were determined by simulation with the program PERCH[17] and give an indication of the real value with a deviation of ±0.2 Hz. Identification of the products was performed using ^{1}H-^{1}H and ^{1}H-^{13}C correlated 2D NMR spectra. Preparative GC was performed with an ATI Unicam 610 series gas chromatograph equipped with an SE 15% 3-m column with the following temperature profile: 10 min 100°C, 10°C/min to 160°C, 15 min 160°C. Mass spectra were recorded with a Finnigan MAT 900 mass spectrometer equipped with a direct insertion probe (EI-MS, 70 eV) or with a Finnigan MAT ITD 700 (EI, 70 eV) coupled to a Packard 438A gas chromatograph equipped with a Chrompack 25-m fused silica column (CP-Sil-5CB; 0.25 mm i.d.) (GC-MS).

General Procedure: Into a dry 250-ml three-necked round-bottomed flask 125 ml of THF was distilled under argon. 0.761 g (5 mmol) of acenaphthylene 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 s. Argon was admitted and sonication restarted. The solution immediately turned dark brown, indicating that the radical anion had been formed. After 5 h 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/liquid 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 min. The mixture was cooled again to −70°C and 5 mmol of alkyl bromide was added. Stirring was continued at room temperature for 30 min after which period the reaction was quenched with water. Addition of light petroleum ether (boiling range 40−60°C), extraction with water, washing with brine, drying with $MgSO_4$ and evaporation of the solvents in vacuo resulted in the isolation of a viscous oil. With a small amount of HCl in acetone, all the products were converted into acenaphthene derivatives. A fraction of each product mixture was separated by means of preparative GC in order to obtain pure material for NMR spectroscopy.

Reaction of the 5-Hydroacenaphthylene Anion with Allyl Bromide: To the 5-hydroacenaphthylene anion, prepared according to the general procedure, 0.866 ml (5 mmol) of allyl bromide was added. Column chromatography on silica gel using light petroleum ether as eluent gave a mixture of mono- and dialkylated products. The mass recovery was 96%.



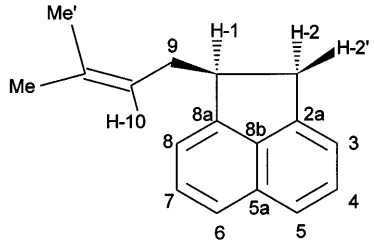
1-Allylacenaphthene (**1a**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.61 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$ = 0.7, $J_{6.8}$ = 1.1, 1 H, 6-H), 7.60 (dddd, $J_{4,5}$ = 8.4, $J_{2.5}$ = $J_{2',5}$ = 1.2, $J_{3,5}$ = 0.7, 1 H, 5-H), 7.46 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1 H, 7-H), 7.45 (dd, $J_{3,4}$ = 6.7, $J_{4,5}$ = 8.4, 1 H, 4-H), 7.30 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 1.6, $J_{6.8}$ = 1.1, 1 H, 8-H), 7.26 (dddd, $J_{3,4}$ = 6.7, $J_{2,3}$ = 0.9, $J_{2',3}$ = 1.0, $J_{3,5}$ = 0.7, 1 H, 3-H), 5.89 (dddd, $J_{10,11}$ = 16.8, $J_{10,11'}$ = 10.3, $J_{9,10}$ = 6.5, $J_{9',10}$ = 7.1, 1 H, 10-H), 5.13 (dddd, $J_{11,11'}$ = −2.2, $J_{10,11}$ = 16.8, $J_{9,11}$ = $J_{9',11}$ = 1.3, 1 H, 11-H), 5.07 (dddd, $J_{11,11'}$ = −2.2, $J_{10,11'}$ = 10.3, $J_{9,11'}$ = $J_{9',11'}$ = 1.4, 1 H, 11′-H), 3.78 (dddddd, $J_{1,2}$ = 8.8, $J_{1,2'}$ = 4.2, $J_{1,9}$ = 4.7, $J_{1,9'}$ = 8.4, $J_{1,8}$ = 1.6, $J_{1,6}$ = 0.7 1 H, 1-H), 3.54 (dddd, $J_{2,2'}$ = −17.5, $J_{1,2}$ = 8.8, $J_{2.5}$ = 1.2, $J_{2,3}$ = 0.9, 1 H, 2-H), 3.10 (dddd, $J_{2,2'}$ = −17.5, $J_{1,2'}$ = 4.2, $J_{2',5}$ = 1.2, $J_{2',3}$ = 1.0, 1 H, 2′-H), 2.67 (dddd, $J_{9,9'}$ = −14.6, $J_{1,9}$ = 4.7, $J_{9,10}$ = 6.5 $J_{9,11}$ = 1.3, $J_{9,11'}$ = 1.4, 1 H, 9-H), 2.54 (dddd, $J_{9,9'}$ = −14.6, $J_{1,9''}$ = 8.4, $J_{9',10}$ = 7.1 $J_{9',11}$ = 1.3, $J_{9',11'}$ = 1.4, 1 H, 9′-H). − ^{13}C NMR ($CDCl_3$): δ = 148.8 (C-2a or C-8a), 144.5 (C-2a or C-8a), 138.7 (C-8b), 136.5 (C-10), 131.5 (C-5a), 127.8 (C-4 or C-7), 127.7 (C-4 or C-7), 122.7 (C-5 or C-6), 122.3 (C-5 or C-6), 119.2 (C-3 or C-8), 118.9 (C-3 or C-8), 116.5 (C-11), 42.6 (C-1), 40.6 (C-9), 36.9 (C-2). − $C_{15}H_{14}$: calcd. 194.1096; found 194.1087. − MS; *m/z* (%): 194 (17), 165 (6), 153 (100), 127 (1), 89 (2).

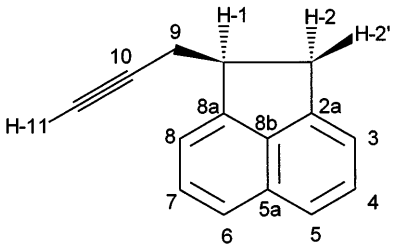


1,1-Diallylacenaphthene (**1b**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.63 (dd, $J_{6,7}$ = 8.1, $J_{6.8}$ < 0.7, 1 H, 6-H), 7.61 (dddd, $J_{4,5}$ = 8.5, $J_{2.5}$ = 1.0, $J_{2',5}$ = 0.8, $J_{3,5}$ < 0.7, 1 H, 5-H), 7.48 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 7.0, 1 H, 7-H), 7.45 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.5, 1 H, 4-H), 7.24 (dd, $J_{7,8}$ = 7.0, $J_{6.8}$ < 0.7, 1 H, 8-H), 7.22 (dddd, $J_{3,4}$ = 6.9, $J_{2,3}$ = 1.4, $J_{2',3}$ = 0.9, $J_{3,5}$ < 0.7, 1 H, 3-H), 5.57 (dddd, $J_{10,11}$ = 16.6, $J_{10,11'}$ = 10.3, $J_{9,10}$ = 6.4, $J_{9',10}$ = 8.1, 2 H, 10-H), 5.04 (dddd, $J_{11,11'}$ = −3.0, $J_{10,11}$ = 16.6, $J_{9,11}$ = $J_{9',11}$ = 1.2, 2 H, 11-H), 4.94 (dddd, $J_{11,11'}$ = −3.0, $J_{10,11'}$ = 10.3, $J_{9,11'}$ = $J_{9',11'}$ = 1.3, 2 H, 11′-H), 3.27 (dd, $J_{2.5}$ = 1.0, $J_{2,3}$ = 1.4, 1 H, 2-H), 3.26 (dd, $J_{2',5}$ = 0.8, $J_{2',3}$ = 0.9, 1 H, 2′-H), 2.55 (ddd, $J_{9,9'}$ = −1.8, $J_{9,10}$ = 6.4, $J_{9,11}$ = 1.2, $J_{9,11'}$ = 1.3, 2 H, 9-H), 2.53 (ddd, $J_{9,9'}$ = −1.8, $J_{9',10}$ = 8.1, $J_{9',11}$ = 1.2, $J_{9',11'}$ = 1.3, 2 H, 9′-H). − ^{13}C NMR ($CDCl_3$): δ = 150.7 (C-2a or C-8a), 143.4 (C-2a or C-8a), 138.4 (C-8b), 134.6 (C-10), 131.2 (C-5a), 127.9 (C-4 or C-7), 127.7 (C-4 or C-7), 123.0 (C-5 or C-6), 122.3 (C-5 or C-6), 119.1 (C-3 or C-8), 118.4 (C-3 or C-8), 117.7 (2 C-11), 50.5 (C-1), 45.4 (C-9), 41.4 (C-2). − $C_{18}H_{18}$: calcd. 234.1408; found 234.1389. − MS; *m/z* (%): 234 (15), 193 (100), 152 (17).

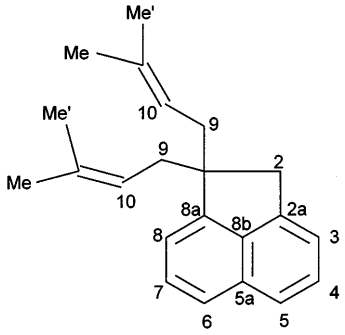
Reaction of the 5-Hydroacenaphthylene Anion with 3,3-Dimethylallyl Bromide: To the 5-hydroacenaphthylene anion, prepared according to the general procedure, 0.576 ml (5 mmol) of 3,3-dimethylallyl bromide was added. Column chromatography on silica gel using light petroleum ether as eluent gave a mixture of mono- and dialkylated product. The mass recovery was 93%.

1-(3-Methyl-2-butenyl)acenaphthene (**2a**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.61 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$ = 0.6, $J_{6.8}$ = 1.0, 1 H, 6-H), 7.60 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$ = $J_{2',5}$ = 1.1, $J_{3,5}$ = 1.0, 1 H, 5-H), 7.45 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1 H, 7-H), 7.44 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.2, 1 H, 4-H), 7.29 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 0.8, $J_{6.8}$ = 1.0, 1 H, 8-H), 7.26 (dddd, $J_{3,4}$ = 6.9, $J_{2,3}$ = $J_{2',3}$ = 1.1, $J_{3,5}$ = 1.0, 1 H, 3-H), 5.28 (ddqq, $J_{10,Me}$ = 1.4, $J_{10,Me'}$ = 1.5, $J_{9,10}$ = 7.1, $J_{9',10}$ = 7.1, 1 H, 10-H), 3.71 (dddddd, $J_{1,2}$ = 8.0, $J_{1,2'}$ = 3.6, $J_{1,9}$ = 6.1, $J_{1,9'}$ = 8.4, $J_{1,8}$ = 0.8, $J_{1,6}$ = 0.6, 1 H, 1-H), 3.54 (dddd, $J_{2,2'}$ = −17.4, $J_{1,2}$ = 8.0, $J_{2.5}$ = 1.0, $J_{2,3}$ = 1.1, 1 H, 2-H), 3.04 (dddd, $J_{2,2'}$ = −17.4, $J_{1,2'}$ = 3.6, $J_{2',5}$ = $J_{2',3}$ = 1.1, 1 H, 2′-H), 2.59 (dddqq, $J_{9,9'}$ = −14.1, $J_{9,10}$ = 7.1, $J_{1,9}$ = 6.1, $J_{9,Me}$ = 0.7, $J_{9,Me'}$ = 0.9, 1 H, 9-H), 2.36 (dddqq, $J_{9,9'}$ = −14.1, $J_{9',10}$ = 7.1 $J_{1,9'}$ = 8.4, $J_{9',Me}$ = 0.7, $J_{9',Me'}$ = 0.9, 1 H, 9′-H), 1.73 (ddd, $J_{10,Me}$ = 1.4,





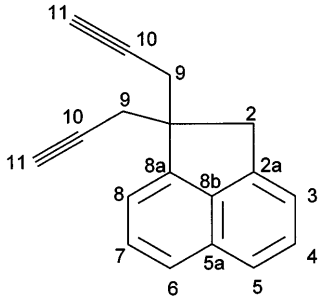
$J_{9,Me}$ = 0.7, $J_{9',Me}$ = 0.7, 3 H, Me), 1.61 (ddd, $J_{10,Me'}$ = 1.5, $J_{9,Me'}$ = 0.9, $J_{9',Me'}$ = 0.9, 3 H, Me′). − ^{13}C NMR ($CDCl_3$): δ = 148.8 (C-2a or C-8a), 144.5 (C-2a or C-8a), 138.7 (C-8b) 131.5 (C-5a), 128.6 (C-4 and C-7), 123.4 (C-10), 123.3 (C-5 or C-6), 123.0 (C-5 or C-6), 119.9 (C-3 or C-8), 119.6 (C-3 or C-8), 44.5 (C-Me, 2 ×), 41.2 (C-1), 38.9 (C-9), 36.5 (C-2). − $C_{17}H_{18}$: calcd. 222.1408; found 222.1476. − MS; *m/z* (%): 222 (27), 184 (8), 153 (100), 127 (5).



1,1-Bis(3-methyl-2-butenyl)acenaphthene (**2b**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.61 (dd, $J_{6,7}$ = 8.2, $J_{6.8}$ = 0.6, 1 H, 6-H), 7.60 (ddt, $J_{4,5}$ = 8.0, $J_{2.5}$ = 0.9, $J_{3,5}$ = 0.5, 1 H, 5-H), 7.46 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 7.0, 1 H, 7-H), 7.44 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.0, 1 H, 4-H), 7.23 (dd, $J_{7,8}$ = 7.0, $J_{6.8}$ = 0.6, 1 H, 8-H), 7.19 (ddt, $J_{3,4}$ = 6.9, $J_{2,3}$ = 1.2, $J_{3,5}$ = 0.5, 1 H, 3-H), 5.01 (ddqq, $J_{10,Me}$ = $J_{10,Me'}$ = 1.4, $J_{9,10}$ = 7.9, $J_{9',10}$ = 6.7, 2 H, 10-H), 3.18 (dd, $J_{2,3}$ = 1.2, $J_{2,5}$ = 0.9, 2 H, 2-H), 2.50 (ddqq, $J_{9,9'}$ = −14.6, $J_{9,10}$ = 7.9, $J_{9,Me}$ = 0.7, $J_{9,Me'}$ = 0.9, 2 H, 9-H), 2.41 (ddqq, $J_{9,9'}$ = −14.6, $J_{9',10}$ = 6.7, $J_{9',Me}$ = 1.2, $J_{9',Me'}$ = 1.5, 2 H, 9′-H), 1.59 (ddd, $J_{10,Me}$ = 1.4, $J_{9,Me}$ = 0.7, $J_{9',Me}$ = 1.2, 6 H, Me), 1.54 (ddd, $J_{10,Me'}$ = 1.4, $J_{9,Me'}$ = 0.9, $J_{9',Me'}$ = 1.5, 6 H, Me′).

Reaction of the 5-Hydroacenaphthylene Anion with Propargyl Bromide: To the 5-hydroacenaphthylene anion, prepared according to the general procedure, 0.446 ml (5 mmol) of propargyl bromide were added. Column chromatography on silica gel using light petroleum ether as eluent gave a mixture of mono- and dialkylated product. The mass recovery was 95%.

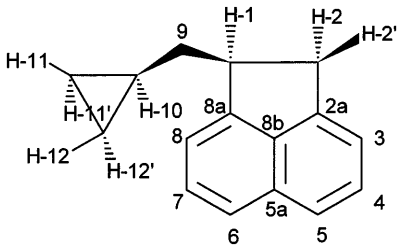
1-Propargylacenaphthene (**3a**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.64 (ddd, $J_{6,7}$ = 8.1, $J_{1,6}$ = 0.7, $J_{6.8}$ = 0.7, 1 H, 6-H), 7.61 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$ = $J_{2',5}$ = 1.1, $J_{3,5}$ = 0.8, 1 H, 5-H), 7.47 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 6.9, 1 H, 7-H), 7.46 (dd, $J_{3,4}$ = 6.8, $J_{4,5}$ = 8.2, 1 H, 4-H), 7.41 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 1.2, $J_{6.8}$ = 0.7, 1 H, 8-H), 7.28 (dddd, $J_{3,4}$ = 6.8, $J_{2,3}$ = $J_{2',3}$ = 1.1, $J_{3,5}$ = 0.8, 1 H, 3-H), 3.90 (ddddd, $J_{1,2}$ = 8.1, $J_{1,2'}$ = 3.5, $J_{9',1}$ = 8.0, $J_{9,1}$ = 6.2, $J_{1,8}$ = 1.2, $J_{1,6}$ = 0.7, 1 H, 1-H), 3.67 (dddd, $J_{2,2'}$ = −17.5, $J_{1,2}$ = 8.1, $J_{2.5}$ = $J_{2,3}$ = 1.1, 1 H, 2-H), 3.22 (dddd, $J_{2,2'}$ = −17.5, $J_{1,2'}$ = 3.5, $J_{2',5}$ = $J_{2',3}$ = 1.1, 1 H, 2′-H), 2.72 (ddd, $J_{9,9'}$ = −16.7, $J_{9,1}$ = 6.2, $J_{9,11}$ = 2.6, 1 H, 9-H), 2.55 (ddd, $J_{9,9'}$ = −16.7, $J_{9',1}$ = 8.0, $J_{9',11}$ = 2.7, 1 H, 9-H), 1.98 (dd, $J_{9,11}$ = 2.6, $J_{9',11}$ = 2.7, 1 H, 11-H). − ^{13}C NMR ($CDCl_3$): δ = 148.8 (C-2a or C-8a), 143.7 (C-2a or C-8a), 138.7 (C-8b), 131.4 (C-5a), 127.9 (C-4 or C-7), 127.8 (C-4 or C-7), 123.3 (C-5 or C-6), 122.4 (C-5 or C-6), 119.3 (C-3 or C-8), 119.1 (C-3 or C-8), 69.2 (C-11), 42.2 (C-1), 37.4 (C-2), 25.4 (C-9). − $C_{15}H_{12}$: calcd. 192.0939; found 192.0933. − MS; *m/z* (%): 192 (18), 153 (100), 126 (2).



1,1-Dipropargylacenaphthene (**3b**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.69 (ddd, $J_{6,7}$ = 2.0, $J_{6.8}$ = 7.0, 1 H, 6-H), 7.65 (ddt, $J_{4,5}$ = 8.5, $J_{2.5}$, $J_{3,5}$, 1 H, 5-H), 7.51 (dd, $J_{6,7}$ = 2.0, $J_{7,8}$ = 7.0, 1 H, 7-H), 7.50 (ddd, $J_{7,8}$ = 7.0, $J_{6.8}$ = 7.0, 1 H, 8-H), 7.49 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.5, 1 H, 4-H), 7.30 (ddt, $J_{3,4}$ = 6.9, $J_{2,3}$, $J_{3,5}$, 1 H, 3-H), 3.46 (s, 2 H, 2-H), 2.83 (dd, $J_{9,9'}$ = −16.7, $J_{9,11}$ = 2.6, 2 H, 9-H), 2.75 (dd, $J_{9,9'}$ = −16.7, $J_{9',11}$ = 2.6, 2 H, 9′-H), 1.98 (dd, $J_{9,11}$ = $J_{9',11}$ = 2.6, 2 H, 11-H). − ^{13}C NMR ($CDCl_3$): δ = 128.0 (C-4 or C-7), 127.7 (C-4 or C-7), 124.0 (C-5 or C-6), 122.7 (C-5 or C-6), 119.5 (C-3 or C-8), 118.9 (C-3 or C-8), 70.4 (C-11, C11′), 43.4 (C-2), 31.5 (C-9), quaternary carbon atom signals not observed. − $C_{18}H_{14}$: calcd. 230.1095; found: 230.1083. − MS; *m/z* (%): 230 (24), 191 (100), 152 (24).

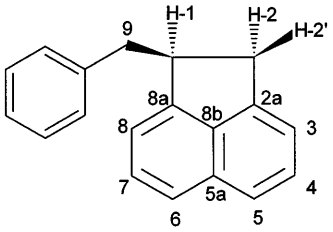
Reaction of the 5-Hydroacenaphthylene Anion with (Bromomethyl)cyclopropane: To the 5-hydroacenaphthylene anion, prepared according to the general procedure using 0.457 g (3 mmol) of acenaphthylene and 0.121 ml (3 mmol) of methanol, 0.357 ml (3 mmol) of (bromomethyl)cyclopropane was added. The crude product was filtered through silica gel with light petroleum ether as eluent. The product mixture consisted of acenaphthene and 1-(cyclopropylmethyl)acenaphthene in a 2:1 ratio. The mass recovery was 96%. The major part of the acenaphthene could be removed by crystallisation from light petroleum ether. Kugelrohr distillation of the oil gave 187 mg (0.9 mmol, 30%) of > 90% pure 1-(cyclopropylmethyl)acenaphthene in the second fraction.

1-(Cyclopropylmethyl)acenaphthene (**4**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.59 (d, $J_{6,7}$ = 8.2, 1 H, 6-H), 7.58 (d, $J_{4,5}$ = 8.2, 1 H, 5-H), 7.44 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.8, 1 H, 7-H), 7.43 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.8, 1 H, 4-H), 7.26 (d, $J_{7,8}$ = 6.8, 1 H, 8-H), 7.25 (d, $J_{3,4}$ = 6.8, 1 H, 3-H), 3.76 (m, 1 H, 1-H), 3.60 (dd, $J_{2,2'}$ = −17.2, $J_{1,2}$ = 8.0, 1 H, 2-H), 3.17 (d, $J_{2,2'}$ = −17.2, $J_{1,2'}$ = 3.5, 1 H, 2′-H), 1.72 (ddd, $J_{9,9'}$ = −13.5, $J_{9,10}$ = 7.2, $J_{1,9}$ = 5.5, 1 H, 9-H), 1.63 (ddd, $J_{9,9'}$ = −13.5, $J_{9',10}$ = $J_{1,9'}$ = 6.33, 1 H, 9′-H), 0.89 (m, 1 H, 10-H), 0.51 (ddd, 2 H, 11-H), 0.19 (ddd, 2 H, 12-H). − ^{13}C NMR ($CDCl_3$): δ = 149.5 (C-2a or C-8a), 144.8 (C-8a or C-2a), 138.6 (C-8b), 131.4 (C-5a), 127.8 (C-6 or C-5), 127.7 (C-5 or C-6), 122.5 (C-7 or C-4), 122.2 (C-4 or C-7), 119.1 (C-8 or C-3), 118.9

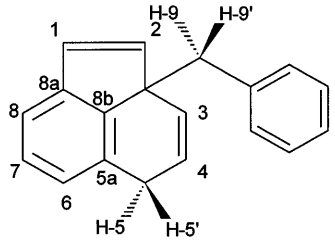


(C-3 or C-8), 44.0 (C-1), 41.5 (C-9 or C-2), 37.5 (C-2 or C-9), 9.4 (C-10), 4.9 (C-11 or C-12), 4.8 (C-12 or C-11). − GC-MS showed one product with mass 208. − MS; *m/z* (%): 208 (100), 166 (17), 153 (70).

Reaction of the 5-Hydroacenaphthylene Anion with Benzyl Bromide: To the 5-hydroacenaphthylene anion, prepared according to the general procedure using 0.457 g (3 mmol) of acenaphthylene and 0.121 ml (3 mmol) of methanol, 0.357 ml (3 mmol) of benzyl bromide was added. Column chromatography on silica gel using light petroleum ether as eluent gave two fractions; the first consisted of acenaphthene and benzyl bromide, the other contained alkylated products. Kugelrohr distillation of the latter gave two fractions and a residue. In the first (largest) fraction 1-benzylacenaphthene and 2a-benzyl-2a,5-dihydroacenaphthylene were present. The major product in the second fraction was 1-benzylacenaphthene. The residue contained at least two dialkylated products.



1-Benzylacenaphthene (**5a**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.61 (ddd, $J_{6,7}$ = 8.2, $J_{1,6}$, $J_{6.8}$, 1 H, 6-H), 7.60 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, 1 H, 5-H), 7.43 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.7, 1 H, 7-H), 7.41 (dd, $J_{3,4}$ = 6.6, $J_{4,5}$ = 8.2, 1 H, 4-H), 7.23 (ddd, $J_{7,8}$, $J_{1,8}$, $J_{6.8}$, 1 H, 8-H), 7.20-7.12 (m, 5 H, H-arom), 7.05 (dddd, $J_{3,4}$ = 6.6, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$, 1 H, 3-H), 4.01 (dddddd, $J_{1,2}$ = 8.1, $J_{1,2'}$ = 2.3, $J_{9',1}$ = 8.9, $J_{9,1}$ = 7.5, $J_{1,8}$, $J_{1,6}$, 1 H, 1-H), 3.47 (dddd, $J_{2,2'}$ = −17.0, $J_{1,2}$ = 8.1, $J_{2.5}$, $J_{2,3}$, 1 H, 2-H), 3.19 (dd, $J_{9,9'}$ = −14.0, $J_{9,1}$ = 7.5, 1 H, 9-H), 3.10 (dddd, $J_{2,2'}$ = −17.0, $J_{1,2'}$ = 2.3, $J_{2',5}$, $J_{2',3}$, 1 H, 2′-H), 2.89 (dd, $J_{9,9'}$ = −17.0, $J_{9',1}$ = 8.9, 1 H, 9-H). $J_{1,6}$, $J_{6.8}$, $J_{7,8}$, $J_{1,8}$, $J_{6.8}$, $J_{2.5}$, $J_{2',5}$, $J_{3,5}$, $J_{2,3}$, $J_{2',3}$, $J_{3,5}$ were observed but not exactly determined. − ^{13}C NMR ($CDCl_3$) : δ = 122.8 (C-6), 122.3 (C-5), 119.2 (C-8 and C-3), 44.63 (C-1), 42.7 (C-9), 37.3 (C-2); assignment of the other C′s was not possible.



2a-Benzyl-2a,5-dihydroacenaphthylene (**5b**): ^{1}H NMR ($CDCl_3$, TMS): δ = 7.39-7.28 (m, 5 H, H-arom.), 7.16 (m, 1 H, 7-H), 6.98-6.94 (m, 2 H, 6-H, 8-H), 6.67 (d, $J_{1,2}$ = 5.5, 1 H, 1-H), 6.58 (d, $J_{1,2}$ = 5.5, 1 H, 2-H), 6.18 (ddd, $J_{3,4}$ = 9.2, $J_{3,5}$ = 0.6, $J_{3,5'}$ = 2.9, 1 H, 3-H), 6.13 (ddd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 6.0, $J_{4,5'}$ = 1.1, 1 H, 4-H), 3.10 (ddd, $J_{5,5'}$ = −20.2, $J_{3,5}$ = 0.6, $J_{4,5}$ = 6.0, 1 H, 5-H), 3.01 (ddd, $J_{5,5'}$ = −20.2, $J_{3,5'}$ = 2.9, $J_{4,5'}$ = 1.1, 1 H, 5′-H), 2.88 (d, $J_{9,9'}$ = −12.6, 1 H, 9-H), 2.61 (d, $J_{9,9'}$ = −12.6, 1 H, 9′-H). − ^{13}C NMR ($CDCl_3$): δ = 142.5 (C-2), 130.0 (C-1), 129.1 (C-4), 128.4 (C-3), 46.2 (C-9), 30.4 (C-5); assignment of the other C′s was not possible.

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