3

Reactivity of the 5-hydroacenaphthylene anion towards alkyl bromides

3.1 Introduction

In Chapter 2 it has been demonstrated that the acenaphthylene dianion reacts with one equivalent of proton selectively at position 5, resulting in the 5-hydroacenaphthylene anion (**1**).[1] Reaction of hydroanion **1** with one equivalent of methyl iodide results in the formation of 1-methyl-1,5-dihydroacenaphthylene in more than 90% yield (Chapter 2).[2]

In this chapter we use the 5-hydroacenaphthylene anion (**1**) 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 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.

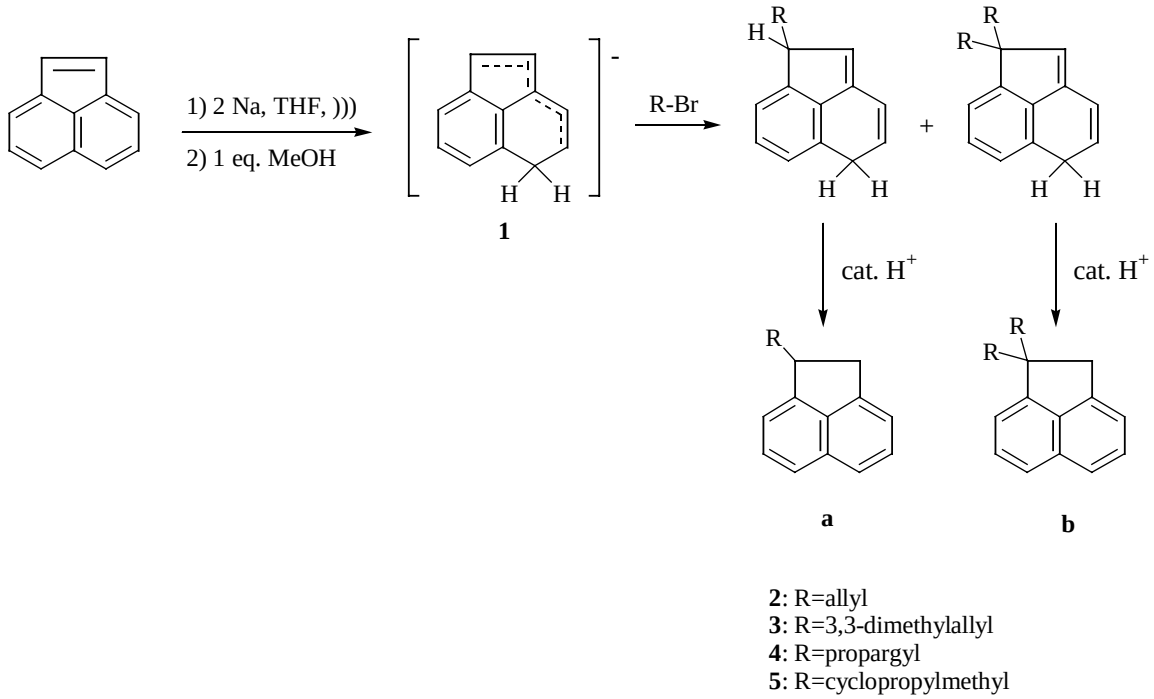
3.2 Results

The 5-hydroacenaphthylene anion was prepared with the procedure outlined in Chapter 2, starting from acenaphthylene, which was converted into its dianion 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 acenaphthylene dianion had been formed. The reaction mixture was cooled to -70ºC 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 -70ºC, 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 (boiling range 40-60ºC) and work-up, 1-allylacenaphthene (**2a**) was obtained as the major product (60% of product mixture). The initially formed product, 1-allyl-1,5-dihydroacenaphthylene, is very unstable and rearranges easily to the acenaphthene derivative − under slightly acidic conditions, even 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 over 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 sufficient amounts of pure products were isolated to measure NMR. By means of NMR techniques the alkylation products were identified as 1-allylacenaphthene (**2a**) and 1,1-diallylacenaphthene (**2b**) (Scheme 1).

The same procedure was used with 3,3-dimethylallyl bromide as electrophile. 1-(3-Methyl-2-butenyl)acenaphthene (**3a**) and 1,1-bis(3-methyl-2-butenyl)acenaphthene (**3b**) 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 (**4a**) and 1,1-dipropargylacenaphthene (**4b**), were separated by preparative GC and could be isolated in a 3:1 ratio (Table 1).



***Scheme 1**: Reaction of **1** with alkyl halides.*

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 and 1-(cyclopropylmethyl)-acenaphthene (**5a**) was obtained.

***Table 1**: Results of the reaction of the 5-hydroacenaphthylene anion with electrophiles. A = acenaphthene, R = substituent*

Electrophile	Overall yield	ratio A : 1-R-A : 1,1-diR-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

3.3 ^{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 (**2a**) (Figure 1) consists of 6 aromatic, 3 olefinic, 3 benzylic and 2 allylic protons.

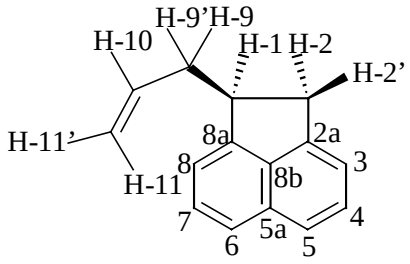


***Figure 1**: 1-Allylacenaphthene (**2a**).*

The aromatic part of the spectrum consists of two separated ABC patterns. Next to the expected ortho and meta couplings H-3 and H-5 show additional small couplings, which could be ascribed to coupling with H-2 and H-2'. A similar coupling can be observed between H-1 and H-6 and between H-1 and H-8. 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 H-1, the cis-coupling being the larger one. H-1 also couples with the distinguishable protons at C-9. 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.[3,4] The dddd's from H-9 and H-9' are due to the coupling with H-10 and allylic coupling with H-11 and H-11'. H-11 and H-11' have coupling constants of 16.8 and 10.3 Hz with H-10, 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 (**3a**) the methyl groups showed allylic couplings with the olefinic proton. The aliphatic part in the spectrum of 1-(cyclopropylmethyl)acenaphthene (**5a**) was too complex to obtain all the coupling constants.

In the 1,1-disubstituted acenaphthenes the molecules have a plane of symmetry. Therefore, both H-2's are identical. The same might be expected for H-9 and H-9', 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.

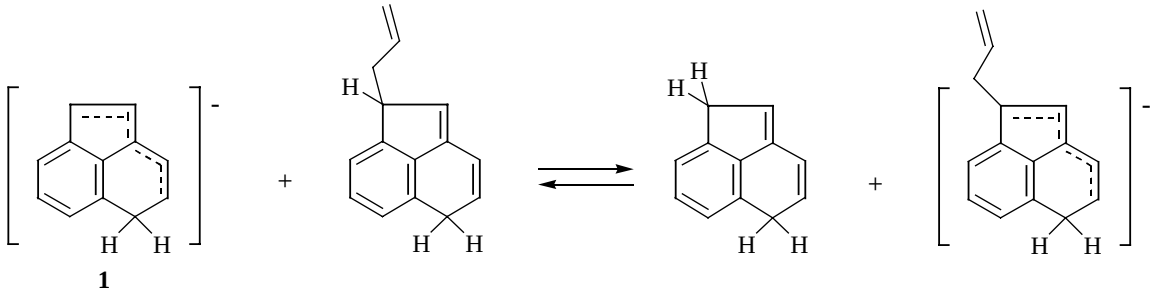
In 1,1-dipropargylacenaphthene (**4a**) a remarkable shift of H-8 towards lower field is observed. This is probably caused by the influence of the π-electrons of propargyl-substituents at C-1. A second deviation from the other spectra are the coupling constants between H-6 and both H-7 and H-8. $J_{6,8}$ increased to 7.0 Hz, $J_{6,7}$ however decreased to 2.0 Hz.

3.4 Discussion

The 5-hydroacenaphthylene anion (**1**) can easily be prepared by addition of one equivalent of methanol to the dianion. The 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 **1**, thus giving 1-allylacenaphthene. In our experiments three products were formed: acenaphthene and 1,1-diallylacenaphthene (**2b**) were isolated next to the expected 1-allylacenaphthene (**2a**). 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 (**2b**) 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 2). Addition of potassium *t*-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 ($pK_a = 25$).

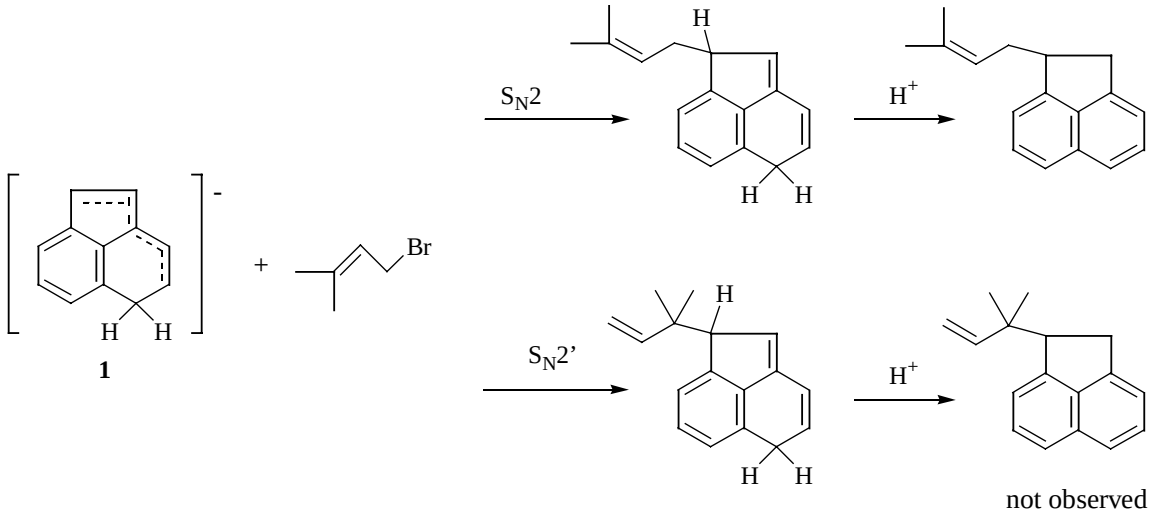
In the reaction with methyl iodide no doubly alkylated product is formed. A possible explanation is that methyl iodide is more reactive towards the hydroanion, thus converting all the hydroanion immediately to the neutral compound and quenching further reaction. The higher reactivity of methyl iodide is in agreement with the influence of the leaving group (iodide vs. bromide) and the substituent (methyl vs. allyl).[5,6]



1

***Scheme 2**: Equilibrium in the reaction of **1** with allyl bromide.*

Allyl bromide can react via 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 3). 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.



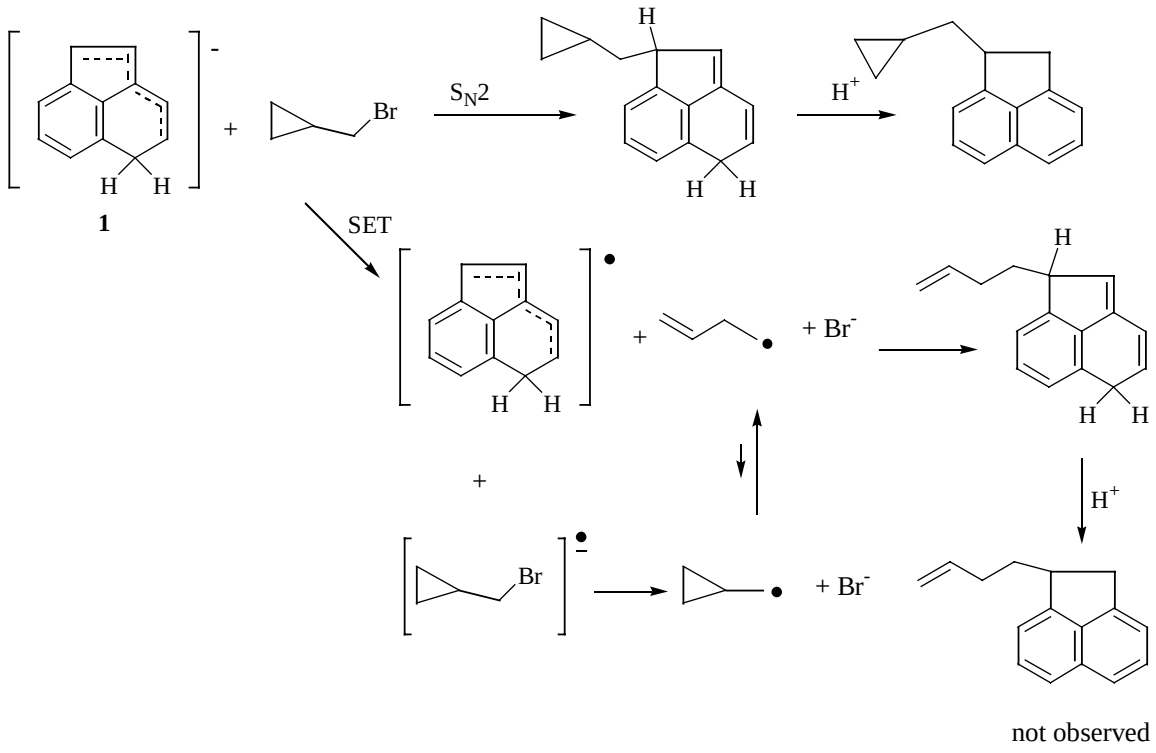
***Scheme 3**: S_N2 and S_N2' mechanism of the reaction of 3,3-dimethylallyl bromide with **1**.*

A similar conclusion can be drawn for the reaction of **1** with (bromomethyl)cyclopropane: if electron transfer were part of the substitution, the cyclopropylmethyl radical would be opened immediately to a butenyl radical (Scheme 4). 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.

These experiments show that the reaction of **1** with alkyl bromides, such as allyl bromide, proceeds via an S_N2 mechanism. The selectivity of this reaction is in accordance with the charge distribution as predicted from the ^{13}C NMR spectrum and quantum mechanical calculations (Chapter 2).

3.5 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 shown to be S_N2 by reaction with dimethylallyl bromide and (bromomethyl)cyclopropane.



***Scheme 4**: Possible pathways for the raction of (bromomethyl)cyclopropane with **1**.*

3.6 Experimental section

General: Acenaphthylene (75%) was obtained from Aldrich and purified by treatment with DDQ and filtration over silica. Allyl bromide, 3,3-dimethylallyl bromide, propargyl bromide and (bromomethyl)cyclopropane were obtained from Acros and used without further purification. Methanol was purchased from Acros, distilled from sodium and stored over molecular sieves (3A, 8-12 mesh). Tetrahydrofuran was purchased from Acros and distilled from sodium and benzophenone immediately before use.

The 300 MHz ^{1}H NMR spectra and 75 MHz ^{13}C NMR spectra were recorded on a Bruker WM-300 spectrometer. The 600 MHz ^{1}H spectrum of 1-propargylacenaphthene was recorded on a Bruker AM-600 spectrometer. All chemical shift 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[7] 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. The numbering of the hydrogen and carbon atoms is indicated in Figure 1.

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

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

General procedure:

Into a dry 250 ml three-necked round-bottomed flask THF (125 ml) was distilled under an atmosphere of argon. Acenaphthylene (0.76 g, 5 mmol) were 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 0°C, a deep green solution was obtained. The flask was then cooled in an ethanol-liquid nitrogen bath to -70°C 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 -70°C and 5 mmol of alkyl bromide were added. Stirring was continued at room temperature for 30 minutes after which period the reaction was quenched with water. Addition of light petroleum (40-60), extraction with water, washing with brine, drying over $MgSO_4$ and evaporation of the solvents *in vacuo* resulted in the isolation of a viscous oil. 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 following the general procedure, allyl bromide (0.87 ml, 5 mmol) was added. Column chromatography over silica using light petroleum as eluent gave a mixture of mono- and dialkylated products. The mass recovery was 96%.

1-Allylacenaphthene (**2a**)

^{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 ,1H, H-6), 7.60 (dddd, $J_{4,5}$ = 8.4, $J_{2.5}$ = $J_{2',5}$ = 1.2, $J_{3,5}$ = 0.7, 1H, H-5), 7.46 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1H, H-7), 7.45 (dd, $J_{3,4}$ = 6.7, $J_{4,5}$ = 8.4, 1H, H-4), 7.30 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 1.6, $J_{6.8}$ = 1.1, 1H, H-8), 7.26 (dddd, $J_{3,4}$ = 6.7, $J_{2,3}$ = 0.9, $J_{2',3}$ = 1.0, $J_{3,5}$ = 0.7, 1H, H-3), 5.89 (dddd, $J_{10,11}$ = 16.8, $J_{10,11'}$ = 10.3, $J_{9,10}$ = 6.5, $J_{9',10}$ = 7.1, 1H, H-10), 5.13 (dddd, $J_{11,11'}$ = -2.2, $J_{10,11}$ = 16.8, $J_{9,11}$ = $J_{9',11}$ = 1.3, 1H, H-11), 5.07 (dddd, $J_{11,11'}$ = -2.2, $J_{10,11'}$ = 10.3, $J_{9,11'}$ = $J_{9',11'}$ = 1.4, 1H, H-11') 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 1H, H-1), 3.54 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2}$ = 8.8, $J_{2.5}$ = 1.2, $J_{2,3}$ = 0.9, 1H, H-2), 3.10 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2'}$ = 4.2, $J_{2',5}$ = 1.2, $J_{2',3}$ = 1.0, 1H, H-2'), 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, 1H, H-9), 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, 1H, H-9').

^{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).
Exact mass calculated for $C_{15}H_{14}$: 194.1096 m/z; found: 194.1087 m/z. MS m/z (%): 194 (17), 165 (6), 153 (100), 127 (1), 89 (2).

1,1-Diallylacenaphthene (**2b**)
^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.63 (dd, $J_{6,7}$ = 8.1, $J_{6.8}$<0.7 ,1H, H-6), 7.61 (dddd, $J_{4,5}$ = 8.5, $J_{2.5}$ = 1.0, $J_{2',5}$ = 0.8, $J_{3,5}$<0.7, 1H, H-5), 7.48 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 7.0, 1H, H-7), 7.45 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.5, 1H, H-4), 7.24 (dd, $J_{7,8}$ = 7.0, $J_{6.8}$<0.7, 1H, H-8), 7.22 (dddd, $J_{3,4}$ = 6.9, $J_{2,3}$ = 1.4, $J_{2',3}$ = 0.9, $J_{3,5}$<0.7, 1H, H-3), 5.57 (dddd, $J_{10,11}$ = 16.6, $J_{10,11'}$ = 10.3, $J_{9,10}$ = 6.4, $J_{9',10}$ = 8.1, 2H, H-10), 5.04 (dddd, $J_{11,11'}$ = -3.0, $J_{10,11}$ = 16.6, $J_{9,11}$ = $J_{9',11}$ = 1.2, 2H, H-11), 4.94 (dddd, $J_{11,11'}$ = -3.0, $J_{10,11'}$ = 10.3, $J_{9,11'}$ = $J_{9',11'}$ = 1.3, 2H, H-11'), 3.27 (dd, $J_{2.5}$ = 1.0, $J_{2,3}$ = 1.4, 1H, H-2), 3.26 (dd, $J_{2',5}$ = 0.8, $J_{2',3}$ = 0.9, 1H, H-2'), 2.55 (ddd, $J_{9,9'}$ = -1.8, $J_{9,10}$ = 6.4, $J_{9,11}$ = 1.2, $J_{9,11'}$ = 1.3, 2H, H-9), 2.53 (ddd, $J_{9,9'}$ = -1.8, $J_{9',10}$ = 8.1, $J_{9',11}$ = 1.2, $J_{9',11'}$ = 1.3, 2H, H-9').
^{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).
Exact mass calculated for $C_{18}H_{18}$: 234.1408 m/z; found: 234.1389 m/z. 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 following the general procedure, 3,3-dimethylallyl bromide (0.58 ml, 5 mmol) was added. Column chromatography over silica using light petroleum as eluent gave a mixture of mono- and dialkylated product. The mass recovery was 93%.
1-(3-Methyl-2-butenyl)acenaphthene (**3a**)
^{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 ,1H, H-6), 7.60 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$ = $J_{2',5}$ = 1.1, $J_{3,5}$ = 1.0, 1H, H-5), 7.45 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.9, 1H, H-7), 7.44 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.2, 1H, H-4), 7.29 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 0.8, $J_{6.8}$ = 1.0, 1H, H-8), 7.26 (dddd, $J_{3,4}$ = 6.9, $J_{2,3}$ = $J_{2',3}$ = 1.1, $J_{3,5}$ = 1.0, 1H, H-3), 5.28 (ddqq, $J_{10,Me}$ = 1.4, $J_{10,Me'}$ = 1.5, $J_{9,10}$ = 7.1, $J_{9',10}$ = 7.1, 1H, H-10), 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, 1H, H-1), 3.54 (dddd, $J_{2,2'}$ = -17.4, $J_{1,2}$ = 8.0, $J_{2.5}$ = 1.0, $J_{2,3}$ = 1.1, 1H, H-2), 3.04 (dddd, $J_{2,2'}$ = -17.4, $J_{1,2'}$ = 3.6, $J_{2',5}$ = $J_{2',3}$ = 1.1, 1H, H-2'), 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, 1H, H-9), 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, 1H, H-9'), 1.73 (ddd, $J_{10,Me}$ = 1.4, $J_{9,Me}$ = 0.7, $J_{9',Me}$ = 0.7, 3H, Me), 1.61 (ddd, $J_{10,Me'}$ = 1.5, $J_{9,Me'}$ = 0.9, $J_{9',Me'}$ = 0.9, 3H, 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, 2x) 41.2 (C-1), 38.9 (C-9), 36.5 (C-2), C-11 was not observed.
Exact mass calculated for $C_{17}H_{18}$: 222.1408 m/z; found: 222.1476 m/z. MS m/z (%): 222 (27), 184 (8), 153 (100), 127 (5).

1,1-Bis(3-methyl-2-butenyl)acenaphthene (**3b**)

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

Reaction of the 5-hydroacenaphthylene anion with propargyl bromide:

To the 5-hydroacenaphthylene anion, prepared following the general procedure, propargyl bromide (0.45 ml, 5 mmol) was added. Column chromatography over silica using light petroleum as eluent gave a mixture of mono- and alkylated product. The mass recovery was 95%.

1-Propargylacenaphthene (**4a**)

^{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 ,1H, H-6), 7.61 (dddd, $J_{4,5}$ = 8.2, $J_{2.5}$ = $J_{2',5}$ = 1.1, $J_{3,5}$ = 0.8, 1H, H-5), 7.47 (dd, $J_{6,7}$ = 8.1, $J_{7,8}$ = 6.9, 1H, H-7), 7.46 (dd, $J_{3,4}$ = 6.8, $J_{4,5}$ = 8.2, 1H, H-4), 7.41 (ddd, $J_{7,8}$ = 6.9, $J_{1,8}$ = 1.2, $J_{6.8}$ = 0.7, 1H, H-8), 7.28 (dddd, $J_{3,4}$ = 6.8, $J_{2,3}$ = $J_{2',3}$ = 1.1, $J_{3,5}$ = 0.8, 1H, H-3), 3.90 (dddddd, $J_{1,2}$ = 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, 1H, H-1), 3.67 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2}$ = 8.1, $J_{2.5}$ = $J_{2,3}$ = 1.1, 1H, H-2), 3.22 (dddd, $J_{2,2'}$ = -17.5, $J_{1,2'}$ = 3.5, $J_{2',5}$ = $J_{2',3}$ = 1.1, 1H, H-2'), 2.72 (ddd, $J_{9,9'}$ = -16.7, $J_{9,1}$ = 6.2, $J_{9,11}$ = 2.6, 1H, H-9), 2.55 (ddd, $J_{9,9'}$ = -16.7, $J_{9',1}$ = 8.0, $J_{9',11}$ = 2.7, 1H, H-9), 1.98 (dd, $J_{9,11}$ = 2.6, $J_{9',11}$ = 2.7, 1H, H-11).

^{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).

Exact mass calculated for $C_{15}H_{12}$: 192.0939 m/z; found: 192.0933 m/z. MS m/z (%): 192 (18), 153 (100), 126 (2).

1,1-Dipropargylacenaphthene (**4b**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.69 (ddd, $J_{6,7}$ = 2.0, $J_{6.8}$ = 7.0 ,1H, H-6), 7.65 (ddt, $J_{4,5}$ = 8.5, $J_{2.5}$, $J_{3,5}$, 1H, H-5), 7.51 (dd, $J_{6,7}$ = 2.0, $J_{7,8}$ = 7.0, 1H, H-7), 7.50 (ddd, $J_{7,8}$ = 7.0, $J_{6.8}$ = 7.0 , 1H, H-8), 7.49 (dd, $J_{3,4}$ = 6.9, $J_{4,5}$ = 8.5, 1H, H-4), 7.30 (ddt, $J_{3,4}$ = 6.9, $J_{2,3}$, $J_{3,5}$, 1H, H-3), 3.46 (s, 2H, H-2), 2.83 (dd, $J_{9,9'}$ = -16.7, $J_{9,11}$ = 2.6, 2H, H-9), 2.75 (dd, $J_{9,9'}$ = -16.7, $J_{9',11}$ = 2.6, 2H, H-9'), 1.98 (dd, $J_{9,11}$ = $J_{9',11}$ = 2.6, 2H, H-11).

^{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 were not observed.

Exact mass calculated for $C_{18}H_{14}$: 230.1095 m/z; found: 230.1083 m/z. MS m/z (%): 230 (24), 191 (100), 152 (24).

Reaction of the 5-hydroacenaphthylene anion with (bromomethyl)cyclopropane:

To the 5-hydroacenaphthylene anion, prepared following the general procedure using acenaphthylene (0.46 g, 3 mmol) and methanol (0.121 ml, 3 mmol), (bromomethyl)cyclopropane (0.36 ml, 3 mmol) was added. The crude product was filtered through silica with light petroleum 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. 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 (**5a**)

^{1}H NMR ($CDCl_3$, TMS) **:** δ = 7.59 (d, $J_{6,7}$ = 8.2, 1H, H-6), 7.58 (d, $J_{4,5}$ = 8.2, 1H, H-5), 7.44 (dd, $J_{6,7}$ = 8.2, $J_{7,8}$ = 6.8, 1H, H-7), 7.43 (dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 6.8, 1H, H-4), 7.26 (d, $J_{7,8}$ = 6.8, 1H, H-8), 7.25 (d, $J_{3,4}$ = 6.8, 1H, H-3), 3.76 (m, 1H, H-1), 3.60 (dd, $J_{2,2'}$ = -17.2, $J_{1,2}$ = 8.0, 1H, H-2), 3.17 (d, $J_{2,2'}$ = -17.2, $J_{1,2'}$ = 3.5, 1H, H-2), 1.72 (ddd, $J_{9,9'}$ = -13.5, $J_{9,10}$ = 7.2, $J_{1,9}$ = 5.5, 1H, H-9), 1.63 (ddd, $J_{9,9'}$ = -13.5, $J_{9',10}$, $J_{1,9'}$ = 6.33, 1H, H-9'), 0.89 (m, 1H, H-10), 0.51 (ddd, 2H, H-11), 0.19 (ddd, 2H, H-12).

^{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).

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