
General conclusions and prospects

10.1 The acenaphthylene dianion

Acenaphthylene can, despite its small size, easily be converted into its dianion with sodium in THF using ultrasonic vibration. It was shown that the dianion can be selectively methylated at position 1 or at position 5, depending on the order of addition of the proton donor and methyl iodide. The most reactive position in the dianion, C-5, is the carbon atom with the highest charge and the largest HOMO coefficient, according to ^{13}C NMR spectroscopy and quantum chemical calculations.

The 5-hydroacenaphthylene anion can be prepared quantitatively from the dianion by addition of one equivalent of methanol. Reaction of the 5-hydroacenaphthylene anion with methyl iodide occurs selectively at position 1.

Until now the acenaphthylene dianion was studied only by NMR spectroscopy. In this thesis the research is extended to the reactivity towards electrophiles and the influence of substituents on the properties of the acenaphthylene dianion.

10.2 Mechanistic aspects

Both the acenaphthylene dianion and the 5-hydroacenaphthylene anion can react via two different mechanisms with electrophiles: $\text{S}_{\text{N}}2$ and SET. The reaction path depends on the HOMO energy of the nucleophile and the LUMO energy of the electrophile. The higher the energy of the HOMO of the nucleophile and the lower the energy of the LUMO of the electrophile, the greater the possibility for SET to occur.

The acenaphthylene dianion reacts selectively with protons and methyl iodide at carbon atom 5 via the $\text{S}_{\text{N}}2$ mechanism. If however an electrophile is used with a lower LUMO energy, such as benzyl bromide or allyl bromide, single electron transfer occurs. Now the reactive particle is the acenaphthylene radical anion. Because acenaphthylene is a non-alternant PAH, the reactivity of the radical anion is different from that of the dianion. The reactivity is now determined by the spin density and the charge density. The substitution via SET is not regioselective and a mixture of products is isolated. The reported lack of selectivity in the reaction of the acenaphthylene dianion with dihaloalkanes by Neumann and Müllen can now be explained as the result of electron transfer.¹

The reaction of the acenaphthylene dianion with bromobenzene is a unique example of a chemically driven $\text{S}_{\text{RN}}1$ reaction. After transfer of one electron from the acenaphthylene dianion to

the bromobenzene and subsequent dissociation of the ensuing radical anion into a bromide ion and a benzene radical, the resulting acenaphthylene radical anion couples with the benzene radical under formation of phenyl substituted acenaphthenes.

The 5-hydroacenaphthylene anion reacts with most alkyl bromides via the S_N2 mechanism. Substitution proceeds selectively at position 1 in the acenaphthylene skeleton. If however the reduction potential of the electrophile is low enough, SET can occur. An SET reaction, such as with benzyl bromide, results, next to the 1-substituted acenaphthene, in the formation of the novel 2a-substituted product. The products are formed in a 1:1 ratio.

The reaction of the 5-hydropyrene anion with benzyl iodide and *n*-propyl iodide gave also substitution at the quaternary position C-3a.^{2,3} The hardness-softness of the electrophiles was assumed to be the cause of the change in regioselectivity. However, also in this reaction electron transfer might play an important role.

Prospects:

The reactions of the acenaphthylene dianion and the 5-hydroacenaphthylene anion with a variety of electrophiles have provided a much better insight into the mechanism of reductive alkylation. Electrophiles can now be ordered with respect to their possibility to give electron transfer. Comparison with other electrophiles allows to predict how a reaction will proceed. A similar approach can be used to study the reductive alkylation of other PAHs and to predict the reactivity of their anions towards electrophiles.

It will be worthwhile to further investigate the use of dianions of PAHs in $S_{RN}1$ reactions.

10.3 Influence of substituents

For the first time the effects of substituents on the reduction and reductive alkylation of acenaphthylene have been studied. Electron-withdrawing substituents as the cyano or the nitro group lower the reduction potential, whereas methyl and methoxy groups (electron donors) increase the reduction potential. Next to the character of the substituent, its position influences the ease of reduction of the acenaphthylene derivative.

The cyano group has an enormous influence on the charge distribution and the reactivity of 1- as well as 5-cyanoacenaphthylene. In the 1-cyanoacenaphthylene dianion the charge is drawn into the five-membered ring. This is established by ^{13}C NMR and *ab initio* calculations. The reaction with methyl iodide takes place at position 1 and, surprisingly, at the nitrogen of the cyano group. Protonation of the 1-cyanoacenaphthylene dianion results, via a 1,2-H-shift, in the thermodynamically most stable hydroanion: 1-cyano-2-hydroacenaphthylene anion.

The charge distribution in the 5-cyanoacenaphthylene dianion is also perturbed by the cyano group and protonation takes place at position 1 exclusively. The resulting 5-cyano-1-

hydroacenaphthylene anion reacts at positions 2 and 5. Reaction at carbon atom 5 leads, after elimination of HCN, to the formation of 5-methylacenaphthylene.

The methyl group exerts a much smaller effect on the reactivity of the acenaphthylene dianion. In both 1- and 5-methylacenaphthylene dianion the highest charge remains located at carbon atoms 5 and 6. However, the methyl group induces asymmetry in the acenaphthylene dianion and this leads to a difference in reactivity of the formerly equivalent positions.

Prospects:

The cyano group has a large effect on the reactivity of the acenaphthylene dianion. It will be interesting to investigate the influence of the cyano group on dianions of other PAHs. Also, the investigation of the effect of less electron-withdrawing groups on the acenaphthylene dianion would help to obtain a better understanding of reductive alkylations. The introduction of a methoxy group might have a larger effect than that of a methyl group. Next to influencing the charge distribution, the methoxy group might increase the energy of the HOMO of the dianion so much that already with methyl iodide an SET reaction would occur.

10.4 Synthetic aspects

The 5-hydroacenaphthylene anion was used in reactions with a wide variety of electrophiles and in this way many novel compounds were synthesised. Alkyl, allyl, propargyl, benzyl, cyanoalkyl, alkyl esters and alkylthio substituents could easily be introduced at position 1 of acenaphthene. The selective synthesis of 1,1-disubstituted acenaphthenes is now possible by using less reactive electrophiles (e.g., allyl bromide) or by addition of a strong base to the reaction mixture.

Reaction of the acenaphthylene dianion was used for the synthesis of interesting compounds such as phenylacenaphthylenes. Although mixtures of products are formed, many of these products cannot be prepared in other ways.

Reactions of the dianions and hydroanions of substituted acenaphthylenes with methyl iodide provide an easy way for the synthesis of novel substituted products, which cannot be prepared selectively by any classical synthetic route. Examples of these products are 1-cyano-1-methylacenaphthene and 5-cyano-2-methylacenaphthene.

Prospects:

The use of a wider variety of electrophiles combined with the use of substituted acenaphthylenes in reductive alkylations will lead to the selective synthesis of a wide range of novel products. The bifunctional electrophiles can be used to extend the existing acenaphthylene skeleton with a new ring.

10.5 Quantum chemical calculations

The development of new easy-to-use computer programs makes it possible for every organic chemist to perform quantum chemical calculations. However, if the results of semiempirical calculations for anions of PAHs are compared to the experimental results, it must be concluded that these calculations can only be used as rough estimations. This might be due to the complex structure of the anions with an excess of electrons. Better results are obtained with *ab initio* calculations. Comparison of experimental and calculated chemical shifts learns that the calculations give a good estimation of the ^{13}C NMR chemical shifts. The charge distribution can be determined by the Mulliken Population Analysis. However, in the MPA the overlap integral is divided equally over two neighbouring carbon atoms and this gives large deviations for the quaternary carbon atoms. Therefore, it is advisable to use the Natural Population Analysis (NPA).

Prospects:

For an even better estimation of the electron density and thus the charge distribution, the calculations should include configuration-interaction, larger basis sets, and diffuse functions. Furthermore, many factors, such as counter ions, solvent, concentration and temperature, which have hitherto been neglected in the calculations should be considered. Progress in computer capacity and calculation systems makes it easier to take these factors into account in the future.

In the calculation, only the starting situation is regarded. The charge and HOMO coefficient distributions in the dianion or hydroanion are used to predict the most reactive positions. However, also the final state and the transition state may play an important role in the reaction path. Therefore, attempts should be made to calculate the entire reaction path.

10.6 References

¹ G. Neumann, K. Müllen *Chimia* **1985**, 39, 275-276

² C. Schnieders, K. Müllen, W. Huber *Tetrahedron* **1984**, 1701-1711

³ R. Brandsma, C. Tintel, J. Lugtenburg, J. Cornelisse *Synth. Commun.* **1985**, 91-93