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REDUCTIVE TRANSFORMATIONS-14. REGIOSELECTIVE ADDITION OF CARBANIONS TO THE "AROMATIC" PYRENE ISOMER DICYCLOPENTA(ef,kl)HEPTALENE[1]

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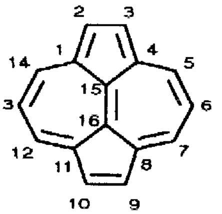
Abstract We report on a LUMO-controlled nucleophilic addition to the pyrene isomer 1 Treatment of 1 with organometallic reagents and subsequent quenching of the resulting monoanionic intermediates yield bridged [14]annulenes

As we reported earlier[2] trans-15,16-dialkyl-1,4,8,11-ethanediylidene[14]annulenes with $R^1=R^2$ are readily available via reductive alkylation of dicyclopenta[ef,kl]heptalene (1)[3] The introduction of bulky groups and the access to unsymmetrically substituted derivatives ($R^1 \neq R^2$), however, meet with problems Of special interest in the search for an alternative annulene synthesis is the alkylation of aromatic hydrocarbons such as naphthalene,[4] anthracene or perylene[5] by nucleophilic additon of alkyllithium compounds

Herein, we describe that the nucleophilic additions of various carbanions to 1 and subsequent quenching of the resulting monoalkyl anions with electrophiles proceed with good yields and high regioselectivity

The title reaction of isopyrene 1 with organometallic species is carried out in analogy to Hafner and his coworkers, who have described the addition of alkyllithium to azulene[6] In a typical experiment 1 is treated in THF-solution with an excess of the organometallic reagent at 0°C



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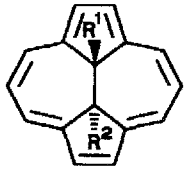

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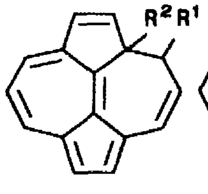

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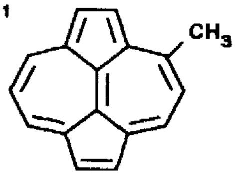

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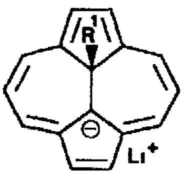

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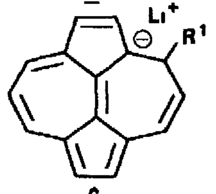
	R^1	R^2		R^1	R^2
a	n-butyl,	methyl	f	phenyl,	methyl
b	n-butyl,	trimethyl silyl	g	methyl,	methyl
c	t- butyl,	methyl	h	allyl,	methyl
d	t-butyl,	t-butyl	i	benzyl,	methyl
e	t-butyl,	n-butyl bromide	k	ethyl,	ethyl



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To the resulting dark red solution of the monoalkyl monoanion 5 is then added an electrophile leading to the dialkylated product 2 By this simple method a multitude of novel annulenes[7] are easily synthesized as given in Table 1 The following observations have been made

Table 1

Nucleophile	Electrophile	Products compd (%)	 compd (%)
methyllithium	methyl iodide		**4** 40
n-butyllithium		**2a** 66	
n-butyllithium	$(CH_3)_3SiOSO_2CF_3$	**2b** 60	
t-butyllithium	methyl iodide	**2c** 65	
t- butyllithium	t- butyl chloride	**2d** 4	
t-butyllithium	1,4-dibromobutane	**2e** 56	
phenyllithium	methyl iodide	**2f** 8	**3f** 58
trimethylstannyllithium		**2g** 17	
allyllithium		**2h** 70	
benzyllithium		**2i** 81	
benzylmagnesium chloride	methyl iodide	**2i** 17	**3i** 60
ethylmagnesium bromide	ethyl bromide	**2k** 78	

(i)- The reaction of **1** with t-butyl-, n-butyl-, allyl-,and benzyllithium and subsequent quenching with methyl iodide as described above lead to the corresponding [14]annulenes **2** The use of methyl- and phenyllithium, however, causes another product distribution

(ii)- In the reaction of **1** with phenyllithium and further electrophilic alkylation with methyl iodide mainly a perimeter-attacked product **3** is observed The corresponding [14]annulene **2** can only be detected as a side-product The structure of **3** was proven by an NOE–NMR experiment of the methyl-phenyl-substituted compound **3f** The methyl group at position 4 is close to the protons at positions 3 and 5, with the signal of the latter occurring at δ 4 10, which is characteristic for the resonance of a benzylic proton

(iii)- Upon addition of methyllithium to **1** and quenching with methyl iodide one obtains the monosubstituted product **4** Thus an addition-elimination mechanism seems to be favored in which the intermediate monoalkyl derivative **6** undergoes an elimination of lithium hydride to form **4**

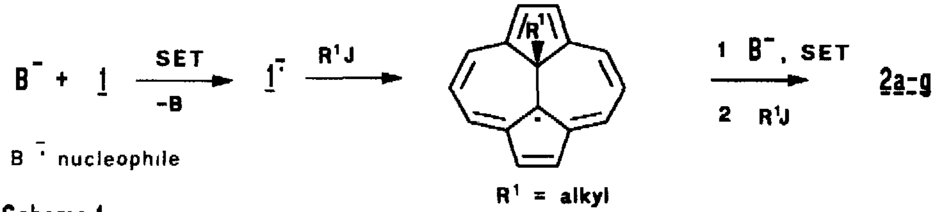
(iv)- A surprising result is the formation of annulene **2g** when trimethylstannyllithium is applied as nucleophilic species and methyl iodide as electrophilic species An incorporation of the trimethylstannyl group is not observed

(v)- The reaction of **1** to the dialkylated product **2** succeeds also with Grignard compounds The addition of ethylmagnesium bromide to **1** and quenching of the resulting ethylmonoanion with, for example, ethyl bromide affords the [14]annulene **2k** in high yield (78%) The insertion of benzylmagnesium chloride as nucleophile in the reaction of **1** gives - in contrast to the use of benzyllithium - preferentially attack at the perimeter with **3** as the main product The [14]annulene **2** is only obtained in a yield of 17% This may be due to the sterically pretentious transition state formed with the benzyl Grignard compound

For many nucleophilic reactions of organolithium or -magnesium compounds with aromatic hydrocarbons single-electron-transfer (SET) pathways are reported[8,9] Evidence for a SET-process is also found upon alkylation of the dianion $\mathbf{1}^{2-}$ [10] This electrophilic reaction, in which a radical monoanion is proposed as intermediate, gives rise to a very similar product distribution as observed here Therefore we made an attempt to detect eventual radical anions in the reaction of **1** with different organometallic species by EPR spectroscopy

Addition of organometallic reagents such as t-butyllithium to the isopyrene results in formation of a stable radical anion. The intense EPR spectra and high-resolution ENDOR spectra yield proton hyperfine couplings of 0.426 ($H_{5,7,12,14}$), 0.10($H_{2,3,9,10}$) and 0.06 mT($H_{6,13}$). The assignment of the hyperfine couplings to the proton positions is based on HMO/McLachlan[11] calculations. From these results and a comparison with the literature[12] the radical could be identified as the monoanion radical of isopyrene.

The detection of high concentrations of isopyrene radicals suggests SET processes to be involved since the corresponding anions of the monoalkyl derivatives **5** and **6** should be EPR silent. With trimethylstannyllithium the product can only be explained by a SET reaction. We suppose that the reagent B^- acts solely as reducing reagent according to Scheme 1. Halogen-metal exchange between trimethylstannyllithium and methyl iodide and addition of the latter to **1** can safely be excluded since reaction of **1** with methyllithium/methyl iodide does not provide **2g**.



Scheme 1

The product distribution in the other cases does not allow to differentiate between nucleophilic addition and a SET reaction via radical species. It is generally assumed that the tendency to SET processes should increase with increasing basicities of the carbanions.[13]

In order to explain the regioselective attack upon **1** and the formation of different products **2**, **3**, and **4** with different nucleophiles we considered the relative reactivity of alkyllithium compounds. If the latter are treated with triphenylmethane and the reaction is monitored by UV/vis absorbtion measurements the following reactivity scale is obtained:[14] benzyllithium > allyllithium > n-butyllithium > phenyllithium > vinyllithium > methyllithium. A similar reactivity sequence has been obtained for resonance-stabilized organolithium compounds, when used as initiators of the polymerization of activated olefins.[15]

Within the same sequence we observe that the yield of **3** (and **4**, respectively) increases and the yield of **2** decreases: the more reactive carbanions preferentially attack the central bridge positions of **1**, while apparently the less reactive species methyl- and phenyllithium attack the perimeter of **1**. It is not clear from the above results, however, whether the regioselective formation of either **2** or **3** (**4**), which depends on a proper choice of the nucleophile, relates to the relative importance of a SET process.

According to a simple HMO/McLachlan calculation[11] the LUMO of isopyrene **1** possesses the highest AO coefficients at the centers 15 and 16 and the second highest AO coefficients at centers 5, 7, 12 and 14. The formation of either **2** or **3** upon nucleophilic attack at either C_{15} or C_5 can, thus, be considered as a LUMO-controlled process. It is also possible from the MO model to predict the position for the subsequent electrophilic attack upon the monoanions **5** and **6**. Indeed, the quenching of **5** and **6** with electrophiles occurs at the centers of highest local π-charge, i e at C_{16} for **5** and C_4 for **6** The regioselectivity of the title reaction can, thus, be treated in a similar fashion as the reductive alkylation of **1**, i e the kinetically controlled reaction of the dianion $\mathbf{1}^{2-}$ with electrophiles

In conclusion, we can carry out carefully directed syntheses of new bridged [14]annulenes and of perimeter alkylated olefinic products The control of the reaction is based upon the choice of the organometallic reagent, but only LUMO-controlled" reaction products are accessible Thus the regioselectivity of the nucleophilic addition to **1** can be rationalized by a consideration of the frontier orbital

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