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Novel π-structures via electron transfer processes—from spectroscopy to synthesis

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Abstract - Electron transfer reactions of unsaturated hydrocarbons can afford stable structures which appear extremely unfavorable on electrostatic grounds. The spectroscopic studies of the ionic π-systems, in particular of the prevailing π-charge distributions, suggest synthetic applications which are remote for the corresponding neutral compounds. Representative examples of reductive alkylations and of reductive σ-bond formations (cleavages) are discussed.

INTRODUCTION

The significance of electron transfer reactions in organic chemistry has been documented in quite different areas of research since these processes occur as crucial steps e.g. (i) in biochemical transformations (ref. 1), (ii) in the electrochemical generation of organic electron storage devices (ref. 2), or (iii) as an alternative mechanistic pathway in S_N reactions (ref. 3).

Towards a unified view of electron transfer processes in unsaturated hydrocarbons we investigated the following sequence of reactions leading to highly charged π-systems:

$$A^{2+} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{+\cdot} \underset{-e}{\overset{e}{\rightleftharpoons}} A \underset{-e}{\overset{e}{\rightleftharpoons}} A^{-\cdot} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{2-} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{3-\cdot} \underset{-e}{\overset{e}{\rightleftharpoons}} A^{4-}$$

The methods of choice for a study of the ions are cyclic voltametry as well as ESR spectroscopy for paramagnetic and NMR spectroscopy for diamagnetic species. Furthermore, the kinetically controlled attack of electrophilic or nucleophilic reagents is expected to proceed at the position of the highest π-charge density in the intermediate ion. The site of highest charge, as determined spectroscopically, is the basic information for the design of novel regioselective reactions (ref. 4).

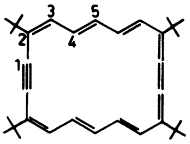
In an attempt to survey the chemistry of delocalized carbanions the following chapters will be dealt with:

1) Novel π-Structures in Delocalized Carbanions - a crucial aspect, thereby, is the subtle balance of electron-electron repulsion and conjugative stabilization;
2) Regioselective Reductive Alkylations - the examples chosen here constitute a straightforward route to novel annulenes;
3) Redox-active Oligomers - which are produced upon reductive alkylation procedures;
4) Electron Transfer Induced Formation or Cleavage of σ-bonds - with the synthesis and transformation of semibullvalenes as a typical example.

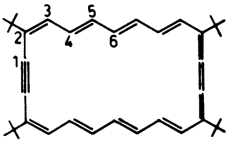
1 NOVEL π-STRUCTURES IN DELOCALIZED CARBANIONS

Rigid perimeter systems such as Nagakawas bisdehydro[4n+2]annulenes (e.g. 1 - 3) (ref. 5) are appropriate model systems to modify the π-electron configuration within an intact σ-frame and to test theoretical predictions. We succeeded in creating an extremely broad sequence of redox reactions ranging from the (paramagnetic) radical cation to a (diamagnetic) tetraanion (ref. 6).

The experimental techniques for the preparation and handling of these species, in particular the spectroscopic control of the reduction, have been described by us elsewhere (ref. 6). A delicate aspect, however, is the reliable structure proof of an exotic species such as a tetraanion. In order to avoid misinterpretations one must refer to a combination of spectroscopic and chemical evidence (ref. 7, 8): (i) reoxidation at any stage of the reduction sequence yields the starting material, (ii) quenching experiments chemically prove the number of extra-charges in the ions, (iii) the ^1H and ^{13}C NMR spectra indicate the intact molecular framework, and (iv) cyclovoltametry reveals the number of electron transfer steps.



1



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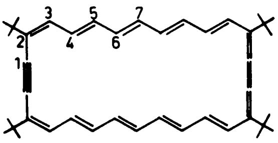
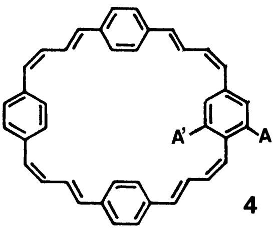


3

The diatropism of the neutral compounds 1 - 3, as measured by the large shift difference of inner and outer protons, decreases with increasing ring size. In accord with theoretical predictions, there is a pronounced tendency toward π-bond fixation (ref. 9). The tetraanions, again constituting (4n+2)π-systems, are strongly diatropic, too, but their diatropism does not decrease.

There is an energetic argument which supports the description of the highly charged tetraanions as π-bond delocalized and, perhaps, conjugationally stabilized systems. In the cyclovoltagram the waves corresponding to the dianion, trianion and tetraanion formation are separated by less than 0.1 V. In benzenoid compounds the waves for monoanion and dianion formation are separated by about 0.5 V (ref. 10) which finding appears reasonable from electrostatic arguments. Consequently, if in the annulene case there is no significant change of solvation enthalpies and entropies, the increasing electron-electron repulsion must be partly compensated by some conjugational stabilization.

The formation of highly charged, π-bond delocalized perimeter structures might have been anticipated in 1 - 3, it is certainly a surprise in macrocyclic cyclophanes such as 4 (ref. 11). The neutral compound must be looked at as some diphenylbutadiene analogue, and the ^1H chemical shifts are, indeed, typical for benzene and olefinic units. In the dianion (ref. 12) one observes an extreme shielding of protons inside the macrocycle and deshielding of outer protons (see formula). Clearly, one has to invoke additional peripheral ring current effects.



4

$4^{2-}/2Li^+$:

$\delta_H(A) = 12.1$

$\delta_H(A') = -9.1$

The neutral compound, in a formal sense, incorporates a 32(= 4n)π-perimeter, each benzene ring contributing a butadiene moiety to the π-periphery. The dianion, indeed, constitutes a true diatropic 34(= 4n+2)π-perimeter.

Another unprecedented carbanion structure is found in compound 5^{2-}/2Li$^+$ (ref. 13, 14), an example of the long elusive bishomocyclooctatetraene dianion. The ^{1}H and ^{13}C NMR data support its description as a symmetric, π-bond delocalized, diatropic species. However, an energetic consideration is more revealing. The cyclovoltametric control of the reduction of 5 is shown in Fig. 1.

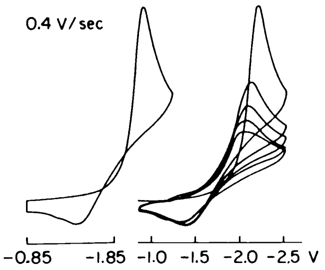
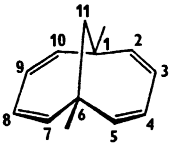


FIG. 1



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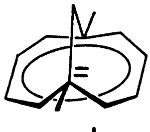


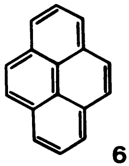
2Li$^+$

The simulation of the current-potential curves indicates that the 2-electron reduction proceeds via the relatively rare ECE-mechanism. Thereby, the first reversible redox step (E-step) is followed by an irreversible chemical step (C-step). One might look at this process as a conformational change of the radical anion by which the through-space interaction of the butadiene basis orbitals is improved. As a consequence of the resulting conjugational stabilization the second redox step occurs at a more positive potential than the first one. That is, inspite of the inherent Coulomb effect of the charge the second electron is transferred with greater ease than the first one. This finding is in accord with the expected homoconjugation.

To conclude, charged π-systems often differ significantly from their neutral counterparts and are prone of adopting extremely surprising, unprecedented structures.

2 REGIOSELECTIVE REDUCTIVE ALKYLATIONS

What is the chemical significance of the above structural description of delocalized carbanions? A key question is whether the charge of the corresponding ions can be localized at certain carbon centers. As a consequence the kinetically controlled addition of electrophiles would allow one to bring in reagents in a regioselective fashion. This would be of particular value if there were no equivalent reaction of the neutral compound.



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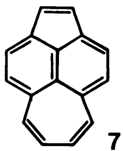

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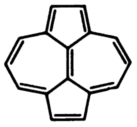

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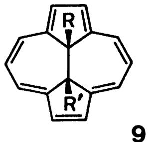


9

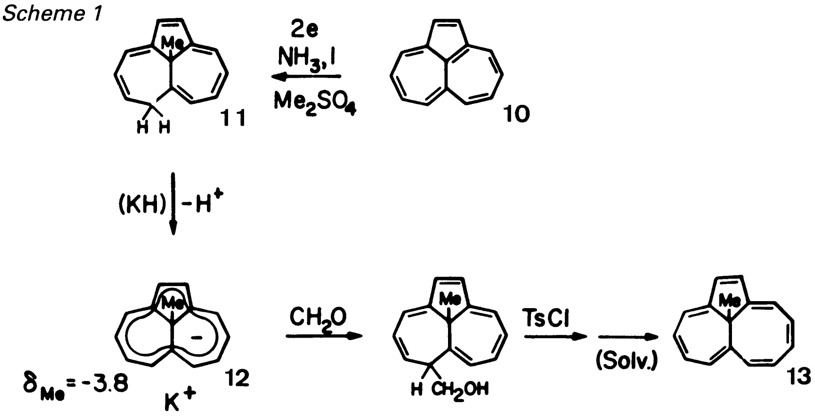
a : R = R' = CH_3
b : R = CH_3, R' = H

Consider, pyrene (6) and its well known isomers 7 and 8. Conventional methods do not allow one to attack the carbons of the inner ethylene bridge. How can one make use of ionic intermediates to achieve that goal?

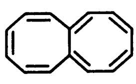
The spectroscopy of the corresponding dianions, again, creates a striking result which is unexpected in view of electrostatic arguments: in $7^{2-}/2Li^+$ the charge is essentially localized in the periphery, the ^{13}C-signals of the inner ethylene carbons are shifted downfield (with respect to the neutral compound) by 45 ppm. In the isomeric dianion $8^{2-}/2Li^+$ the charge is localized in the inner ethylene moiety, the corresponding resonances are shifted upfield by 50 ppm. This result can be rationalized by the underlying orbital scheme: the LUMO's of 6 and 7, but not that of 8, possess a nodal plane through the bridge (ref. 15). The chemical application of this structural finding is straightforward, since only in the case of 8^{2-} the addition of electrophiles will proceed at the inner ethylene moiety and thus allow one to produce bridged [14]annulenes such as 9 (ref. 16). The above route constitutes a simple one-step annulene synthesis which uses an easily accessible (according to Hafners work (ref. 17)) starting compound and which can readily be modified to introduce different bridging groups.

For the tricyclic 14π-system aceheptylene (10) (ref. 18) one predicts the highest π-charge density of the corresponding dianion at the central carbon and, indeed, upon going from the neutral compound to the dianion its resonance is shifted upfield by 60 ppm (ref. 19, 20). Not surprisingly, therefore, methylation produces a mixture of diadducts in which one methyl group has always entered at the angular position (ref. 21). In liquid ammonia as solvent the reductive methylation affords only one single hydromethyl adduct 11 in 80% yield (ref. 19). Deprotonation of 11 (see Scheme 1) gives rise to a first 14 π-monocyclic anion (12), a higher homologue of the cyclopentadienylium anion. Hydroxymethylation of the anion with formaldehyde and solvolytic ring enlargement of the corresponding tosylate produces a new type of a π-perimeter (13), a [14]annulene being bridged by one methin group (ref. 21).

Scheme 1



The above concept of reductive transformations comprises the simple MO-search for suitable substrates, the experimental verification of the π-charge distribution via a spectroscopic study of the ionic intermediates and, finally, the unconventional chemical application. Further examples of this technique, such as the transformation of octalene (14) into the conformationally mobile [14]annulene 15, have been reported by us (ref. 22).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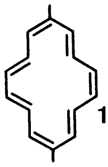
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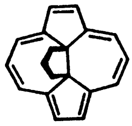
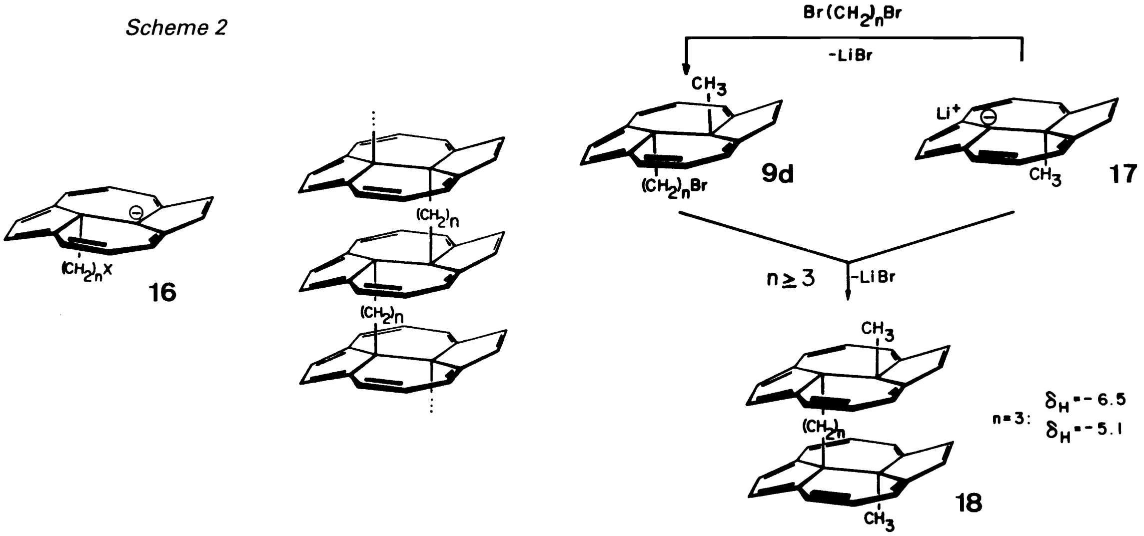

9c

3 REDOX-ACTIVE OLIGOMERS

The reductive transformations outlined above can be applied to the synthesis of redox-active oligomeric and polymeric compounds. If the dianion 8^{2-} is reacted with 1,n-dihaloalkanes one obtains the cyclization product 9c which deviates much more from planarity than its trans-isomer (ref. 16). A closer look at the intermediate haloalkyl substituted monoanion (16) of the isopyrene reveals (see Scheme 2) that it possesses both electrophilic and nucleophilic character. It is therefore prone of undergoing a polymerization which should produce a completely new type of multilayered π-systems with a face-to-face arrangement of the separate entities. The difference to multilayered cyclophanes is that the former type has its bridging group inside the π-cloud instead of outer linkages as in cyclophanes. Toward the synthesis of the double-layer one generates the monoanion 17 via the deprotonation of 9b and reacts it in a simple alkylation process with the different bromides 9d.

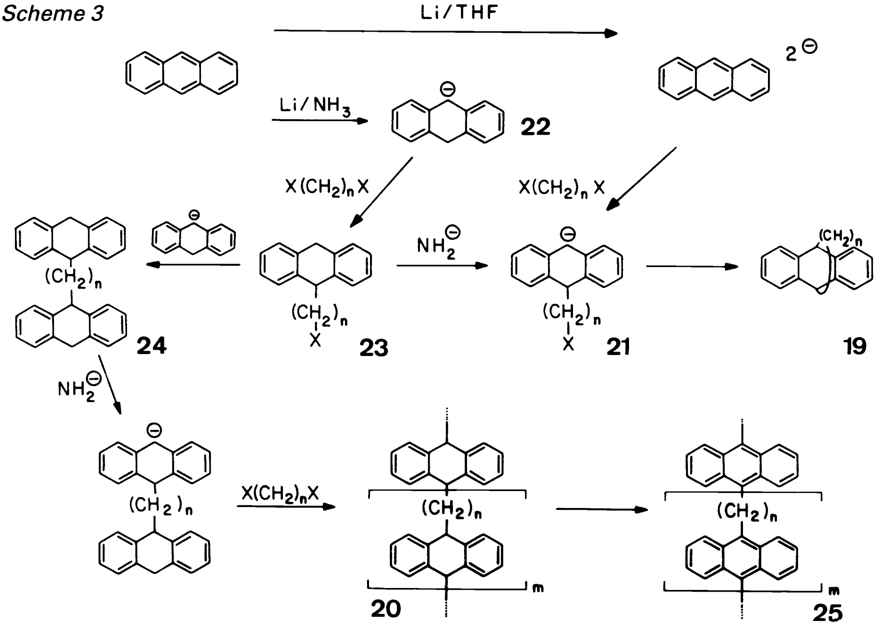
Scheme 2



If air is carefully excluded, the double-layers 18 are formed in nearly quantitative yields (see Scheme 2) (ref. 23). The distance of the π-systems and thus their through-space interaction can be controlled via the polymethylene linkage. The shielding of the bridge protons inside the π-clouds of two diatropic rings is witnessed by their extreme highfield resonances. More important within the present context is the fact that, starting from the double-layers, one can create and characterize the complete redox sequence ranging from a monoanion to a tetraanion. The spectroscopic (ref. 23) and electrochemical data (ref. 24) leave no doubt that there is, indeed, a pronounced through-space interaction of the ionic π-units. Thus, e.g. in the radical anion, the spin density appears to be delocalized over both moieties.

The above coupling reaction can afford different types of polymeric hydrocarbons with separate, electroactive redox centers. The well-known anthracene dianion is a most useful substrate for the application of bifunctional alkylation agents. When its dilithio salt in THF is reacted with dihalopropanes one obtains a 1,4-diadduct (19) as major product. If the reductive alkylation is performed in liquid ammonia, however, one only observes a polymerization process (ref. 25, 26). This reaction affords long chain molecules (20) (see Scheme 3) in which dihydroanthracene moieties are linked by flexible alkane groups (ref. 27). The mean molecular weights of the soluble products, which are determined via vapor pressure osmometry, can be controlled by varying the experimental conditions such as the concentration of the alkylating agent and the relative amount of ammonia and ether. Concerning the mechanism of the polymerization reaction and, in particular, the factors discriminating between monomeric and polymeric products, it is seen from Scheme 3 that the reaction can be initiated by introducing different starting compounds and applying different experimental techniques (ref. 26). Always the haloalkyl substituted monoanion 21 constitutes the key intermediate.

Scheme 3



In one alternative, anthracene is reduced with lithium in liquid ammonia. The NMR-spectroscopic control of this step indicates that the dianion does not persist but is rapidly protonated by the solvent to yield the monohydro anion 22 (ref. 28). Alkylation and subsequent deprotonation by the amide provides the monoanion 21. The latter can cyclize to monomeric "bridged" products or react with a second species of the same kind. Essential for high yields of polymer, however, is the reaction between 23 and the monoanion 22 which, at an early stage of the reaction, is present in high concentration. The cyclization product is, therefore, not observed. In a similar fashion, the monomer is only observed in THF if the dianion concentration is kept extremely low. Evidence for the initial dimerization step in liquid ammonia comes from the following: high yields of the polymer are also achieved by reacting the tetrahydrodianthrylalkane (24) with an excess of amide and by quenching with one equivalent of dihaloalkane. In contrast, the best yields of the monomeric cyclization products 19 are obtained when the pure haloalkyl dihydroanthracene 23 is treated with amide in liquid ammonia. Under these conditions the potential side reactions are surpressed.

The detection of the molecular ions of the polymer 20 via field desorption mass spectrometry provides the single homogeneous mass distribution which can be compared with the osmometric data. As expected from the mechanism of the reductive polymerization the samples contain 3 different structures depending on whether anthracene and/or alkyl groups constitute the terminals of the chain.
The dehydrogenation of the poly(dihydroanthrylene-propylene) is accomplished by reaction with sulphur at 200^{o}C, the resulting polyanthrylene systems 25 give correct elemental analysis.

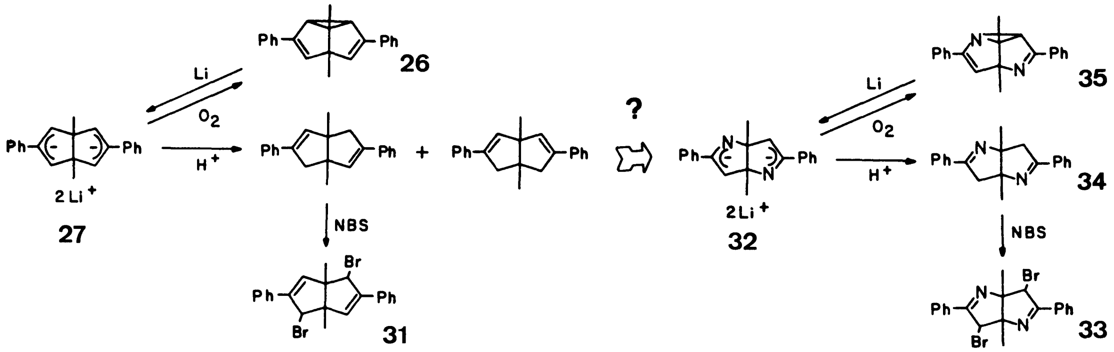
For the sake of comparison we have prepared some oligomeric model compounds: the α,ω-dianthrylalkanes 25 (m=1) as well as the corresponding trianthrylene species (with m=2) (ref.

29). The hydrocarbons were then submitted to electron transfer reactions. The structure proof of the resulting ions rested upon quenching experiments, cyclovoltametric evidence and upon the ESR and NMR spectra. The ESR spectra of the radical anions of 25 (m=1, n=2, 3, 4) (ref. 30) leave no doubt that for the appropriate ion pairing the spin density can be delocalized over both π-entities, and the same holds true for the higher homologue with m=2. Likewise, the singlet dianion of e.g. dianthrylethane is π-charge delocalized and shows a striking similarity with the dianion of the structurally related anthracenophane in which the through-space interaction of the electro-active π-systems is enforced by their face-to-face arrangement. Furthermore, while previous experiments reported in the literature suggested ready σ-bond cleavages of the molecules upon reduction, we succeeded in preparing and characterizing even the tetraanions as thermally stable species. In extrapolating these findings to the related polymer two aspects are important: the compound can transform into highly charged species and there is an electronic interaction along the chains.

4 ELECTRON TRANSFER INDUCED FORMATION OR CLEAVAGE OF σ-BONDS

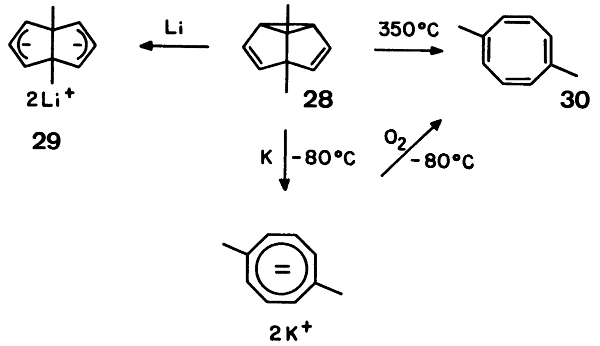
We have considered various examples of valence isomerizations such as Berson-Willcott-rearrangements and 2+2-cycloadditions and demonstrated the rate enhancement brought about by an electron transfer (ref. 31, 32). It follows from kinetic measurements by ESR and NMR spectroscopy that the isomerization of a radical anion can proceed by a factor of up to 10^{15} faster than that of the neutral compound.

Semibullvalenes constitute another interesting class of compounds for which one can test the possibility of electron transfer induced skeletal rearrangements.



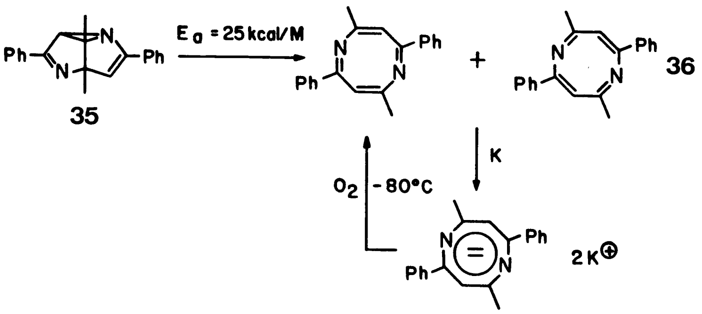
Reduction of the diphenylsemibullvalene 26 with lithium (ref. 33, 34) causes a σ-bond cleavage; the dianionic product 27 can be considered as a symmetric bisallyl-type system (ref. 35, 36). (The occurrence of the highest π-charge density at the terminal allyl centers is inferred from the ^{13}C-chemical shifts. At temperatures below ca. -80°C there occurs a dynamic process which implies the interconversion of covalent dimeric structures (ref. 37).)

What is the chemical use of this facile decyclization of the strained semibullvalene? Paquette prepared specifically substituted cyclooctatetraenes via thermolysis of their semibullvalene isomers (ref. 38). The reaction of the 1,5-dimethylsemibullvalene 28 with lithium affords the bisallyl-type dianion 29. With potassium, however, one obtains the related cyclooctatetraene dianion 30^{2-} which can be reoxidized to the neutral compound (ref. 36). The advantage of the smooth ionic process is obvious when realizing that the thermolysis of the neutral compound proceeds at temperatures in excess of +350°C.



In a formal sense, the dilithiosemibullvalenes 27 and 29 can be regarded as the reduction products of the symmetric transition state of the Cope rearrangement. This structural relationship suggested the question if the dianions could be used synthetically in order to achieve neutral semibullvalenes with extremely rapid valence isomerization or, probably, with a bishomoconjugated ground-state. This problem has for long been a challenge for synthetic and theoretical efforts. Dewar suggested that the 2,6-diazasemibullvalene should constitute the extreme case in that it possesses a non-classical ground-state structure (ref. 39). In our approach toward an example of this yet unknown compound we realized that 26 could be formed by oxidation of 27 and by reductive debromination of 31. The diazaanalogue of 27, namely the dianion 32, was known in the literature (ref. 40).

When we conducted the reductive debromination of 33 (easily accessible from 34) with highly active lithium under strict exclusion of air and, most importantly, under NMR spectroscopic control, we obtained compound 35, a first example of a 2,6-diazasemibullvalene. Spectroscopic monitoring of the reaction is essential since the extremely labile product decomposes rapidly upon further metal contact. The bond theoretical problem can easily be solved since there is a dynamic line broadening in the ^{13}C-NMR spectra of 35 at low temperatures. This finding leaves no doubt that there occurs an extremely rapid degenerate Cope rearrangement and that there is a normal "double-minimum" energy profile (ref. 35).



The same methods afford the related bromo- and dibromo semibullvalenes which undergo a non-isodynamic or isodynamic Cope rearrangement, respectively. At modest temperatures, much lower than the related hydrocarbons, the diazasemibullvalene 35 rearranges into the first stable 1,5-diazocine 36 (ref. 41) which possesses a tub-shaped eight-membered ring and forms stable double-bond isomers.

The essence of the present survey of electron transfer reactions is the fruitful interplay of simple bond-theoretical, spectroscopic and preparative approaches. The resulting highly-charged species, if they are handled properly and if their structures are fully elucidated, allow for novel synthetic applications which seem remote for the corresponding neutral compounds.

ACKNOWLEDGEMENTS

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