DOI: 10.1002/anie.200803476

Stable Five-Membered-Ring Allenes with Second-Row Elements Only: Not Allenes, But Zwitterions

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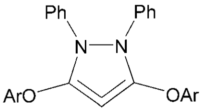
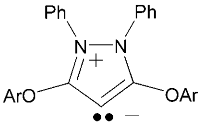
cyclic allenes · pyrazolium ions · zwitterions

In a recently published Communication, Lavallo, Dyker, Donnadieu, and Bertrand[1] try to convince the reader that there are isolatable 1,2-cyclopentadienes, derived from a pyrazole with donor substituents in positions 3 and 5, which have the electronic structure of allenes and which are persistent at room temperature, for example **1a**. As we show herein, the compound given the Lewis formula **1a** does not exhibit the typical properties of allenes. On the basis of overwhelming evidence, the compound in question has to be the zwitterion **1b**.



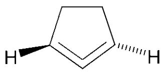
1a



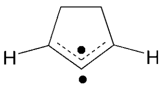
1b

Ar = 2,6-Dimethylphenyl

Owing to the short lifetime of six-membered cyclic allenes that contain only second-row elements,[2] the persistence of an allene with the structure **1a** at room temperature would be most surprising. In general, experimental findings regarding five-membered cyclic allenes are extremely rare.[2,3] The unsubstituted 1,2-cyclopentadiene has recently been investigated with quantum-chemical methods.[4] According to these results, the ground state has an allene character and is thus best represented by formula **2a**, because the carbon atoms C1, C2, and C3 do not lie in one plane with the carbon and hydrogen atoms bound to C1 and C3. However, the energy of **2a** turned out to be only slightly more favorable ($<1\,\text{kcal}\,\text{mol}^{-1}$) than that of the diradical **2b**, whose five carbon atoms and the hydrogen atoms of C1 and C3 are coplanar. The species **2b** is the transition state for the enantiomerization of **2a**.[4]

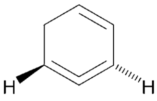


2a

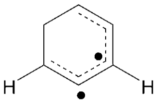


2b

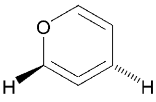
To date, the influence of π-donor substituents at the allene moiety of **2a** has not been studied, but quantum-chemical calculations of such effects are known in the case of six-membered cyclic allenes. The barrier to enantiomerization of 1,2,4-cyclohexatriene (**3a**) amounts to approximately 10 kcal mol^{-1}.[5–7] At variance with **3a**, the transition state of this process, that is the diradical **3b**, proved to be an achiral species, whose atoms, except for the hydrogen atoms at C6, lie in one plane.



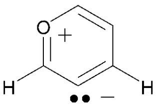
3a



3b

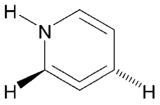


4a

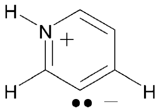


4b

The oxygen atom as a π-donor substituent at the allene subunit of 1-oxa-2,3,5-cyclohexatriene (**4a**) has the structural consequence that the allene system and its substituents deviate much less from the coplanar arrangement than in **3a**.[6,7] The cause for this effect can be seen in the structure of the transition state for the enantiomerization of **4a**, namely the zwitterion **4b**, which is derived from the pyrylium ion, is completely planar, and higher in energy than **4a** by only 1–3 kcal mol^{-1}. This small energy difference imparts substantially the properties of **4b** to **4a**, specifically a geometry approaching that of **4b** and a polar character.[6,7]



5a



5b

In 1994, it was established that for pyridine derivative **5**, the ground state is the zwitterion **5b**.[8] As more extensive studies confirmed, the allene structure **5a** does not represent an energy minimum.[7,9]

If the results of the calculations of **4** and **5** are extrapolated, the coplanar arrangement of the three carbon atoms of the alleged allene system of formula **1a** and its two nitrogen and oxygen atoms has to be expected. According to the X-ray structure analysis performed by Lavallo, Dyker, Donnadieu, and Bertrand, this is perfectly true.[1] Given this geometry, the Lewis formula **1a** cannot be correct, as the bonding conditions typical for allenes cannot be met. Which Lewis formula is then valid for the molecule in question instead of **1a**?

Both the extrapolation of the bonding relationships of **4** and **5** and the reaction producing the substance, that is

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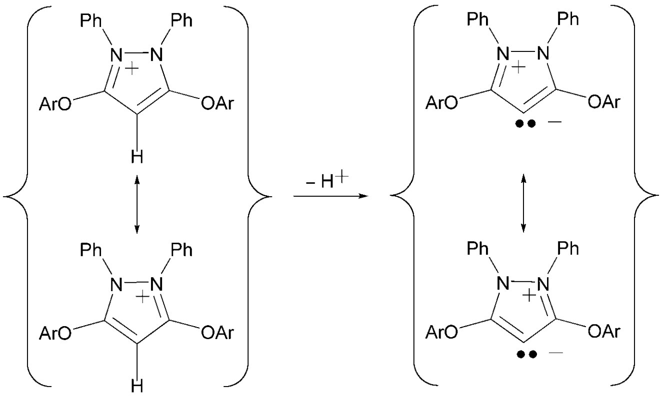
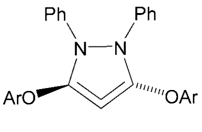


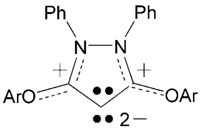
6 **1b**

the deprotonation of the pyrazolium ion **6**,[1] provide a clear-cut answer: we are dealing with the zwitterion **1b**, derived from pyrazole.

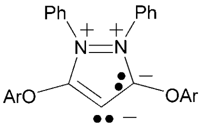
The conversion of **1b** into the genuine allene structure **1c** requires only the shift of the lone pair of the carbon atom onto a nitrogen atom. Please note that because of the different geometry **1c** is not identical with **1a**. Since this reorganization of the electrons is accompanied by the loss of the aromatic character of **1b** and the build-up of an enormous strain energy (ca. 45 kcal mol^{-1}, approximately corresponding to the strain-energy difference of **2a** and **2b**[4]), a strong preference exists for the retention of the geometry of **1b**, which is predetermined by that of **6**.



1c



1d



1e

The experimental data of the deprotonation product of **6** are perfectly in agreement with the structure **1b**. Accordingly, the ^{13}C NMR chemical shifts are exactly as expected. The length of the bonds C3–C4 and C4–C5 (C1–C2 and C1–C3, respectively, in ref. [1]) are 137.0 and 138.6 pm and thus typical for pyrazolium ions.[10] Because of the mutual steric hindrance of the phenyl groups, the nitrogen atoms accept a slight pyramidalization, which should hardly disturb the aromatic state. Particularly revealing is the C-C-C angle in the five-membered ring, which turned out to be 97.5° and thus significantly smaller than the respective angle in pyrazolium ions (ca. 105°).[10] The origin of this reduction is the electrostatic repulsion that the lone pair at the central carbon atom exerts on the electrons of the σ bonds of that carbon atom. The calculation of the structures **4b** and **5b** indicated this very effect by conspicuously small bond angles of the carbanionic centers.[6,7,9] If **1c** were the correct structure instead of **1b**, the consequence would be a much larger angle, probably as large as that of **2a**, which has been calculated to be 114°.[4]

The contribution of the resonance structure **1d** of **1b** to the ground state of the species can only be determined by valence-bond calculations. Presumably, its weight is smaller than that of the resonance structures **1b** and **1e** because of the presence of two negative charges at C4. Nevertheless, the action of **1b** as a four-electron donor of the **1d** type seems possible, since a strongly electrophilic transition-metal species, after its coordination to the carbanionic center of **1b**, could demand a second electron pair corresponding to an electrophilic attack at C4 of the now present pyrazolium ion, which bears donor substituents in positions 3 and 5.

Received: July 17, 2008

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