

Why is a Vinyl Anion Configurationally Stable but a Vinyl Radical Configurationally Unstable?

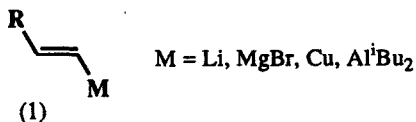
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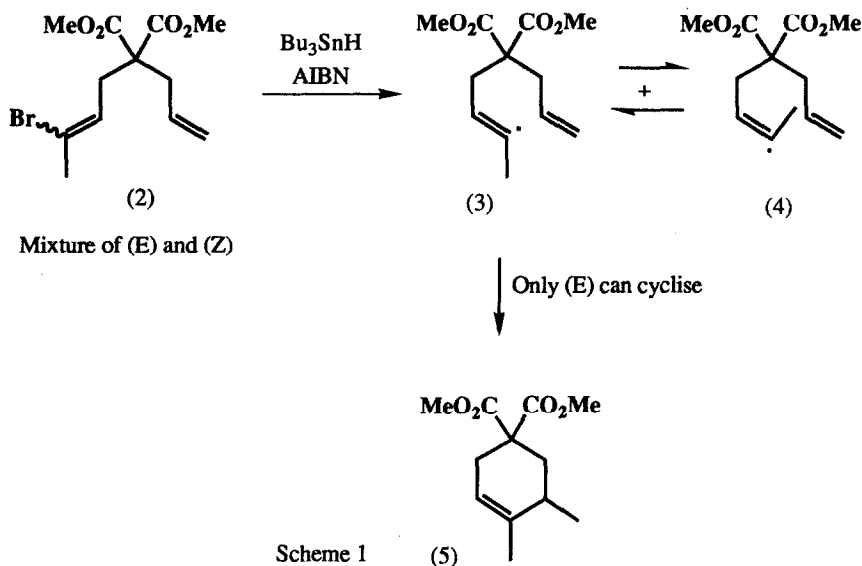
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Abstract A qualitative explanation of the configurational stability of vinyl anions and the configurational instability of vinyl radicals is given.

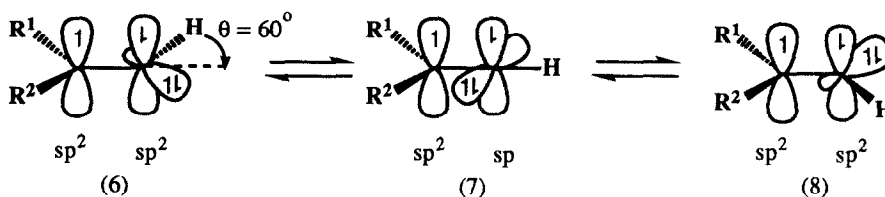
The stereoselective synthesis of (E) and (Z)-olefins is one of the cornerstones of synthetic chemistry. Traditionally this task is achieved using Wittig type olefination reactions. However, more recently the synthesis of configurationally stable vinyl anions has also found wide application.¹ These anions may be prepared by the deprotonation of a suitably activated vinylic proton,² by exchange of a metal for a halogen leading to vinyl magnesium and lithium compounds,³ by transmetallation usually of a lithium for a tributyl tin group⁴ or by the addition of aluminium⁵ or copper⁶ reagents to alkynes. Using these methods configurationally stable metallated alkenes (1) are produced which can be applied in the synthesis of (E) and (Z) olefins. In some cases vinyl anions can invert especially when substituted by a sulfoxide group⁷ but these examples are exceptional.



The pioneering work of Stork⁸ on vinyl radicals has demonstrated their remarkable synthetic utility.⁹ In all this work vinyl radicals are produced from vinyl bromides and chlorides with tributyltin hydride. The vinyl radicals generated were found to invert rapidly between (E) and (Z) isomers, an example is shown by the representative example in Scheme 1. The mixture of (E) and (Z) isomers (2) was converted into the mixture of vinyl radicals (3) and (4) but only the (E) can cyclise to six-membered ring (5).

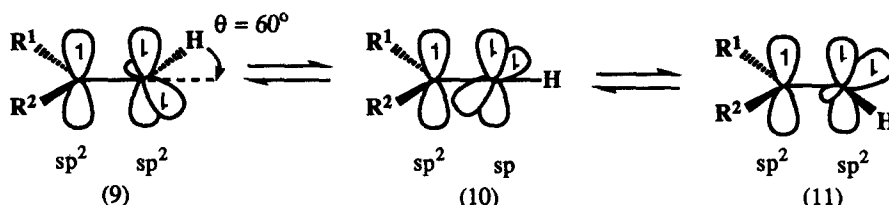


If we consider the anion $\text{R}^1\text{R}^2\text{C}=\ddot{\text{C}}\text{H}$ in terms of Valence Shell Electron Pair Domain Theory (VSEPD)¹⁰ we find that there is one double bond domain at the carbanionic centre and two single bond domains from the CH bond and the lone pair; these would be expected to take up a trigonal planar geometry. In the corresponding radical $\text{R}^1\text{R}^2\text{C}=\dot{\text{C}}\text{H}$ one electron has been removed from the lone pair domain of the anion thus reducing the influence of this domain on the molecular geometry. The geometry of the radical carbon will be principally determined by the double bond domain and the single bond domain of the CH bond and therefore this carbon atom should have an approximately linear geometry. If we bear these predictions in mind and now consider a hybridisation picture for the inversion of a vinyl anion and radical we arrive at Schemes 2 and 3.



Scheme 2: The Vinyl Anion

The orbital hybridisation of the anion (6) is unlikely to differ much from the protonated parent. In other words both carbon atoms are reasonably represented as being "sp²" hybridised and hence the "lone-pair" orbital is approximately an sp² hybrid. Any relaxation is likely to increase θ , the angle between the C(1)-H bond and the C-C direction, i.e. $\theta > 60^\circ$. The transition state for inversion is expected to resemble (7), with $\theta = 0^\circ$. In this structure the lone-pair orbital becomes pure 2p_y, which is clearly high in energy relative to the trigonal arrangement in (6) which was predicted to be the most stable geometry form the VSEPD argument given above. This leads to a high energy barrier to inversion for the vinyl anion (6).



Scheme 3: The Vinyl Radical

In marked contrast to vinyl anions, vinyl radicals (9) have moved close to the structure of the "linear" intermediate (10) in agreement with the predicted linear geometry given above and leading to a low barrier to inversion. Indeed some radicals $R_2C=\dot{C}R'$ are actually linear as judged by e.s.r. spectroscopy (eg $R' = Ph, CO_2H$). For the parent vinyl radical, $H_2C=\dot{C}H$, inversion is fast on the e.s.r. time scale at room temperature, the two β -protons being apparently equivalent. On cooling, the asymmetric structure is detected¹¹. From the ^{13}C (1) hyperfine coupling data for the derivative $(HO_2C)CH=^{13}\dot{C}H$,¹² an approximate $p:s$ ratio of 10 is found (after allowing for a small spin polarisation contribution). [Using $A^0(^{13}C)=115$ G and $2B^0(^{13}C)=61$ G and the usual comparative procedure.¹³]

For an AB_2 radical this $p:s$ ratio corresponds to a deviation from linearity of *ca* 15° .¹⁴ This is a highly approximate calculation but it shows that vinyl radicals must have structures that are relatively close to being linear.

These arguments provide a convincing qualitative explanation of the important experimental contrast between the inversion behaviour of vinyl anions and the corresponding radicals.

There is a close analogy with results for carbanions and alkyl radicals, or amines and amine radical cations. R_3C^- and R_3N^- are pyramidal with bond angles less than the tetrahedral value. In contrast, R_3C^\cdot and $R_3N^{+\cdot}$ are planar, as judged from e.s.r. and other forms of spectroscopy. The simplest way of understanding these results is to consider the degrees of orbital hybridisation in the σ -bonding and formally non-bonding (HOMO or SOMO) orbitals. For example, for R_3N^- : the 6 σ -bonding electrons are delocalised onto the R- groups whereas the lone pair is almost confined to nitrogen. Since the 2s orbital is far deeper than the 2p manifold, it is favourable for the lone-pair to acquire more s-character than the σ -bonding electrons. [This is far more marked for H_3P^- molecules, where the lone-pair is almost pure 3s, the bond angle being close to 90° .] However, for $R_3N^{+\cdot}$ one electron has been removed. It is now more favourable for the residual "hole" to be in the 2p-manifold than in the 2s-orbital on nitrogen. Hence the radical-cation becomes planar, and the SOMO is the 2p(π) orbital on nitrogen. Exactly the same reasoning explains the configurational stability the vinyl carbanions and the configurational instability of the corresponding radicals.

Conclusion

The configurational stability of a vinyl anion can be understood from the relative instability of intermediate (7) in its inversion process, whereas the corresponding intermediate in the inversion of a vinyl radical (10) is relatively more stable leading to a lower energy barrier to inversion.

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