Tetrahedron Letters No. 12, pp 1073 - 1076, 1978. Pergamon Press. Printed in Great Britain.

PLANAR TETRACOORDINATE CARBON IN A TRANSITION STATE

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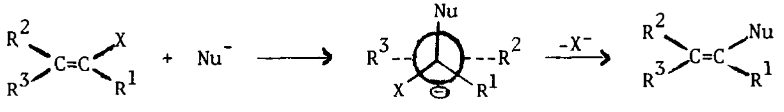
(Received in UK 18 January 1978; accepted for publication 30 January 1978)

Interest in molecules containing planar tetracoordinate carbon increased in recent years. The field has recently been reviewed by Collins, Schleyer, Pople and coworkers,[1] who stated that several of the suggested structures have not yet been synthesized, while the structures of others, especially polylithium compounds, are not known experimentally. They outlined three main effects which help to stabilize a planar tetracoordinate over a tetrahedral carbon. A singlet planar methane is sp^2-hybridized with six bonding electrons in the molecular plane and two non-bonding electrons in a perpendicular p-orbital. Stabilization can be achieved by delocalizing the lone pair by π-conjunction, by providing more electrons to carbon by σ donation and by reduction of the angle around the planar carbon atom by means of small rings. Extensive ab initio calculations revealed several molecules which are more stable in the planar than in the tetrahedral geometry, and others where the energies of the tetrahedral and the planar structures are sufficiently close so that the transition state for the stereomutation of the tetrahedral isomers will involve a tetracoordinate carbon. We wish to indicate that there are examples and stereochemical evidence for a tetracoordinate carbon in the transition state of some $sp^2 \rightarrow sp^2$ substitutions.

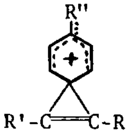
Nucleophilic substitution at an activated vinylic carbon proceeds usually with retention of configuration.[2] Stereoconvergence, i.e., formation of an identical product mixture from both isomers is obtained only when the initial products are unstable,[2] when the leaving group is poor[3] or when the activating group is highly capable of negative charge dispersal.[4] Regardless whether the substitution proceeds in a single step or via an intermediate (eq. 1), the nucleophile attacks from a plane perpendicular to the double bond and the intermediate or the transition state are tetrahedral



(1)

or close to tetrahedral.[2,5] Calculations suggest that the transition state for an in-plane attack is of much higher energy than that for the perpendicular attack.[6] Such a reaction would lead to inversion at the site of substitution with a planar tetracoordinate carbon at the transition state. Although both the S_N2 inversion and the stepwise perpendicular attack[7] are "allowed" processes,[5] inversion in an overall nucleophilic vinylic substitution of an acyclic system was not yet observed.

However, there are two families of vinylic substitutions which proceed with inversion of configuration. The first group includes the formation of charged rings, e.g., **1**-**4** by anchimeric nucleophilic participation by β-sulfur,[8] β-iodine,[9] β-aryl[10] and probably β-bromine[9] in the solvolysis of the appropriate vinylic derivatives (eq. 2, Y = Ar, R''S, I, Br). The second group is the opening of these rings, e.g. thiirenium ions,[8] vinylidenephenonium ions[10] or vinylideneiodonium ions[9] by an external nucleophile Nu⁻ (eq. 3). The stereochemistry of the overall process via both eqs. 2 and 3 is retention of configuration via a double inversion. An alternative double retention process is excluded since ring-closure with retention would lead to the highly improbable trans three membered cyclic olefinic system. By microscopic reversibility the nucleophilic ring-opening should proceed with inversion, although a ring opening with retention via a perpendicular nucleophilic attack[2] is sterically feasible. The observed retention for the overall process excludes this possibility.



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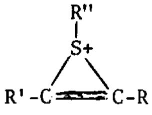

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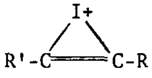

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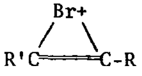

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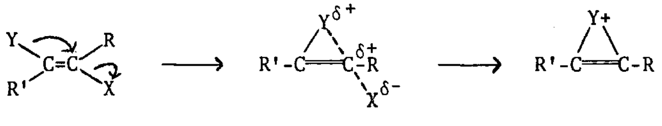

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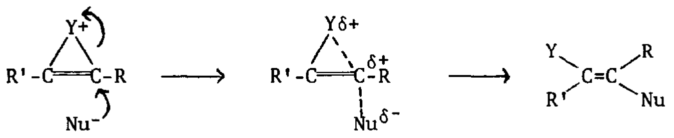
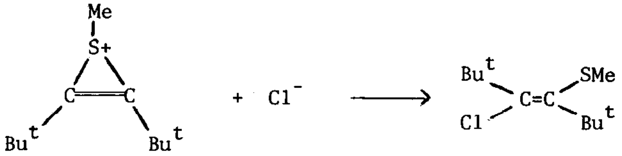


(3)

Three-membered charged rings, e.g. **2** and **4**, are formed also in electrophilic additions of e.g., aryl or alkyl sulfenyl chlorides[8] or bromine[8] to acetylenes. The ring opening leads to trans adducts and is identical with eq. 3, involving a tetracoordinate carbon in the transition state.

Usually the three-membered rings are not detected directly or isolated during the reaction and the evidence for a planar carbon in reactions 2 and 3 depends mainly on the observed retention of configuration in the solvolysis of β-aryl-, β-alkylthio-, β-arylthio- and β-iodo-α-substituted vinylic systems,[8-10] However, several substituted thiirenium ions were isolated[11] and the reaction of 1-methyl-2,3-di-t-butylthiirenium ion with chloride ion which gives the <u>inverted</u> E-1,2-di-t-butyl-2-(methylthio)vinyl chloride (eq. 4) was observed directly.[11b] This supports the extensive evidence



(4)

for the intermediacy of thiirenium ions in the solvolysis of compounds $R''SC(R')=C(R')O_3SC_6H_2(NO_2)_3$-2,4,6.[8]

These ring-opening reactions were previously viewed as part of the vinyl cation chemistry, but when viewed as substitution reactions they raise the problem why a transition state with a planar tetracoordinate carbon becomes more stable than the more common transition state with a tetrahedral carbon in an intermediate. A qualitative analysis is valuable for explaining this remarkable preference. Systems such as **1-4** differ from the ordinary substrates of nucleophilic vinylic substitution in three respects. First, vinylic substitution via tetrahedral transition states proceeds easily with electron poor substrates where the electron-withdrawing β-substituents disperse the negative charge formed in the transition state.[2] The systems involved in ring formation carry electron-donating β-substituents, and in the ring-opening process the electron-deficiency is due to the bridging atom or group. Second, the stereochemistry of nucleophilic vinylic substitution studied so far involved anionic leaving groups, while with **1-4** the leaving group is neutral. Third, on expulsion of the leaving group in the cyclic systems the large strain of these rings is partially relieved, while the cyclic tetrahedral transition state will retain more of the strain of the original system. In terms of the Schleyer-Pople analysis,[1] the planar distortion energy is reduced compared with the tetrahedral one by an enforced reduction of the angle around the planar carbon in the small ring and by delocalizing the lone pair by π-conjunction over the molecular π-orbital of the double bond.

The stereochemistry of nucleophilic vinylic substitution cannot be regarded anymore as stereospecific with retention,[5] but as depending on the nature of the α- and the β-substituents, the charge on the leaving group and its involvement in a ring. The stereochemistry of nucleophilic ring opening of non-charged rings such as substituted oxirene , thiirene and cyclopropenone is therefore an interesting problem, although complications such as nucleophilic attack on the carbonyl carbon of cyclopropenones[12] or loss of the stereochemistry in the substitution of an oxirene due to the formation of an enolate ion, will be encountered. Less strained charged rings were also formed by anchimeric assistance in vinylic solvolysis. A five-membered oxonium ion so formed was attacked on the substituent attached to oxygen[13] but a nucleophilic ring opening of a five-membered chlorolium salt was suggested.[14] The ring opening can lead to a different stereochemical outcome than in reaction 3 as indicated by the formation of a 1:1 mixture of the E- and Z-1-iodo-2-(o-iodophenyl)-2-phenyl-1-hexenes in the opening of the 3-butyl-2-phenylbenziodolium ion with methoxide ion in methanol.[15]

Inversion in the ring opening can still be obtained if the nucleophile approaches the ring at an angle from a direction opposite to that of the leaving group. Intuitively the corresponding non-planar transition state is less likely than a planar transition state, but we want to emphasize that our suggestion for a planar carbon in the transition state should be supported by calculations of the energies of the planar and other transition states for the opening of the three-membered charged rings.

Acknowledgement: I am indebted to Prof. S. Patai and Dr. Y. Apeloig for discussions.

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