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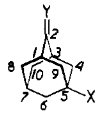
Communications

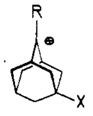
Electronic Aspect of Face Selection in the Oxy-Cope Rearrangement

Summary: We report experiments aimed at defining the electronic effect in the face selection of the oxy-Cope rearrangement. The probe used is a 1,5-hexadiene system having a 5-fluoroadamant-2-ylidene substituent at one terminus. The product ratio shows a clear bias toward bond formation such that the antiperiplanar bond is the more electron-rich one.

Sir: Face selection during addition to trigonal carbon is at the core of stereogenesis. The more obvious steric aspect of face selectivity was the first one studied, in 1952;[1] the possible presence of an electronic effect was not investigated until two decades later.[2] These and other early researches were largely limited to reactions of nucleophiles with carbonyl compounds in which there was no opportunity to study the two contributions separately. A previous report[3] from this laboratory demonstrated that 5-substituted adamantan-2-ones **1**-Y-X could be used as a new and effective probe for the study of electronic effects in the addition of nucleophiles to trigonal carbon. The system is free from steric complications, and it can readily be converted into a host of other substrates for use in probing electronic effects in other types of reactions at trigonal centers.



1-Y-X



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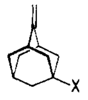

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We determined that with oxygen as Y, electron-donating substituents X direct nucleophiles toward the anti face of the carbonyl group while electron-withdrawing groups direct them toward the syn face. No exceptions have been found to date. We explained our data in terms of the hyperconjugative model of the transition state advocated by Cieplak[4] to explain the well-known preferred axial approach of nucleophiles toward the carbonyl group in cyclohexanones. According to this model, the energy of the activated complex is lowered by hyperconjugation of an antiperiplanar bond with the incipient σ^* orbital (Figure 1). The model is closely related to that proposed by Winstein[5] for the transition state of σ assisted solvolysis; indeed, the behavior of 2-phenyl-2-adamantyl cations **2** clarifies[6] aspects of solvolysis that had long been controversial.[7] In olefins **3**, we find that electron-withdrawing groups X behave exactly the same way toward electrophiles as they do vis-a-vis nucleophiles,[8,9] and the same directive effect is also seen in both thermal cycloaddition and photocycloaddition.[10] Whether the model is defensible on a computational basis or not,[11,12] there is to date no reason to doubt the reliability of the empirical rule that addition to trigonal carbon on electronic grounds is preferred at that face that has the most electron-rich orbital in the antiperiplanar position. As part of a study of substituent effects on the face selectivity in pericyclic reactions, we are now able to show that this rule correctly predicts the principal product in the oxy-Cope rearrangement.

Aldol condensation of **1**-O-H with acetophenone followed by dehydration and addition of allylmagnesium bromide to the resulting enone gives rise to racemic **4**. Treatment of this compound with potassium hydride leads to achiral ketone **5**. In principle, four transition states are possible

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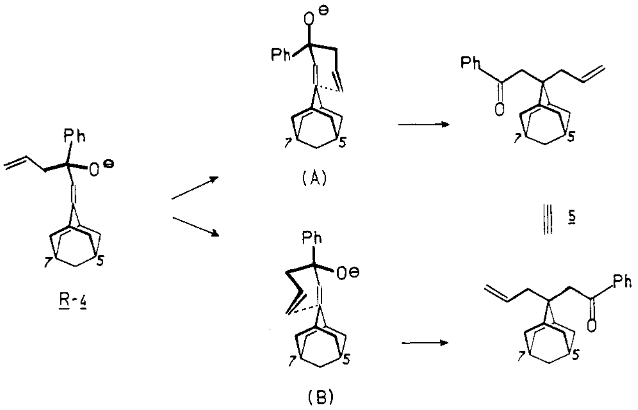
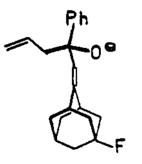
Figure 1. Schematic view of the orbitals involved in the hyperconjugative stabilization of transition states of addition to trigonal carbon.

Scheme I

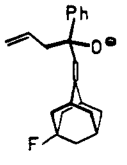


since face selection occurs at both termini. Two of the four are boat-shaped; these are ruled out by Evans' experiments.[13] The other two are chairs that differ in that one (A) has the phenyl group axial and the other (B) has it equatorial (Scheme I; this arbitrarily shows the *R* isomer).

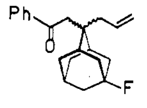
The same synthetic sequence beginning with 1-O-F gives a 50/50 mixture of two diastereomers **6** and **7**, with configurations *RR,SS* and *RS,SR*, respectively; they were quantitatively separated by means of column chromatography. Note that **6** and **7** differ from **4** by a fluoro substituent at C_5 and C_7, respectively. If one follows Scheme I through with this in mind, it can be seen that **6A** and **7B** give *E*-**8**, whereas **7A** and **6B** produce *Z*-**8**. In one of the diastereomers, the steric and electronic effects operate in opposition, in the other, they act in unison. The configurations of the two products *E*- and *Z*-**8** were determined easily be means of the effects of the fluorine atom and of the added shift reagent $Eu(fod)_3$ on the ^{13}C NMR spectra; quantitative analysis of the mixtures showed that one diastereomer gave rise to an *E*/*Z* ratio of 81/19, the other of 36/64. The electronic factor clearly favors syn approach as predicted. With no assumption except that the difference in energy between **A** and **B** is unaffected by whether the fluorine is located at C_5 or C_7, we calculate that the predilection for syn approach amounts to a factor of 1.4, and the steric difference between **A** and **B** causes a rate ratio of 2.6 between the two approaches. As a result, a 50/50 mixture of **6** and **7** would show a net preference for bonding at the fluoro side of nearly 60%.



6 (RR)



7 (SR)



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The secondary question whether **A** or **B** is the sterically preferred transition state is one we can at present not answer definitively, although our extensive ^{13}C NMR studies of **6** and **7** suggest that the one giving the most syn approach is **7** (*RS,SR*; equatorial phenyl). This evidence will be discussed in the full paper; the important conclusion for now is that in this sigmatropic shift, the face selected is that antiperiplanar to the most electron-rich bond. In that regard, the oxy-Cope rearrangement now joins all other additions to trigonal carbon examined to date.

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Man-hua Lin, W. J. le Noble*
Department of Chemistry
State University of New York
Stony Brook, New York 11794

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An Unprecedented Intramolecular Migration of Carbon Groups from Aluminum to an Adjacent Vinylic Center and Its Application to the Synthesis of Stereodefined Olefins

Summary: Hydroalumination of 1-chloro-1-alkynes by sodium trialkylaluminum hydrides furnishes stereo- and regioselectively the respective (*E*)-1-chloro-1-alkenylalanates, which, in the presence of NaOMe, undergo a novel 1,2-migration of a carbon group from Al to the adjacent vinylic center to generate a useful synthesis of di- and trisubstituted olefins of defined geometry.

Sir: Migratory insertion reactions are ubiquitous in organoboron chemistry, representing the most common method for synthesizing carbon–carbon bonds by using boron.[2,3b] On the other hand, this type of 1,2-migration reaction has rarely been observed for the corresponding organoaluminums.[3] Until recently, in fact, the only reported examples of organoaluminums that appear to have undergone migratory insertion are the reaction of organoalanes with diazomethane to yield the homologous alanes[4] and the reaction of lithium chloropropargylide with

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