WHY MOLECULAR FLUORINE ADDS TO ETHYLENES IN A *CIS* FASHION[1)]

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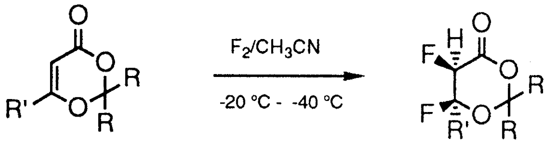
The addition of dilute molecular fluorine to ethylenes proceeds stereoselectively to give the *cis* adducts, and the method has now gained potential synthetic utility for the preparation of a variety of fluorinated compounds. A possible mechanism accounting for this selectivity is proposed based on HOMO-LUMO theory, bond distances, and weakness of F-F bond.

KEYWORDS fluorination; *cis* addition; molecular fluorine; HOMO-LUMO theory

The use of fluorine diluted with inert gas has led to remarkably selective and controllable transformations such as addition to a double bond and substitution at a tertiary carbon,[2)] and provided useful synthetic methods for a variety of fluorinated compounds. Recently, we examined the reactions of 1,3-dioxin-4-ones (**1**) with molecular fluorine (5% F_2/N_2) and obtained the corresponding *cis*-5,6-difluorinated adducts (**2**) in complete stereoselection.[3)]



1 **Chart 1** **2**

It has been well known that fluorine adds predominantly in a *cis*-fashion to ethylenes, even in flexible cases.[4,5)] To the best to the present authors' knowledge, an explanation for this preference has only been proposed by Merritt.[6)] In his proposal, a molecular adduct (**I**) is formed at first which may continue on to products through two competing routes, shown in Chart 2 as paths a and b. A major contribution of complex **I** *via* path a will favor direct *cis* addition and will predominate in cases where the incipient carbonium ion (**II**) is not extensively stabilized.

Reaction of fluorine with steroidal olefins[4)] and the dioxinones[3)] proceeded *via* path a to give solely the *cis* adducts. On the contrary, indene,[7)] acenaphthylene,[7)] and *cis*- and *trans*-propenylbenzenes[6b)] afforded, in addition to the *syn* addition products, the *trans* adducts in

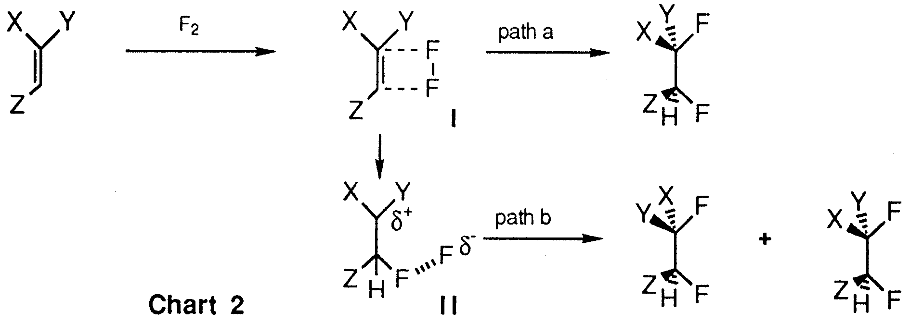


Chart 2

significant amounts. Merritt reasoned that the concomitant formation of the *trans* adducts is due to path b, which is favored by stabilization of the carbonium ion (**II**) by a phenyl group (X or Y = Ph).

In this paper, we will propose an explanation, based on theoretical grounds, for why **I** is formed at the first stage in the fluorination of ethylenes by molecular fluorine and how **I** is transformed in the final *cis* adducts.

Due to Fukui's theory, HOMO-LUMO interaction between two molecules has the major role in determining the stability of the interacting species. Previously, Houk[8)] reported HOMO and LUMO energies of a variety of ethylenes by surveying the experimental data. Thus, HOMO energies were obtained from photoelectron spectroscopic study and LUMO energies from polarographic reduction potentials and charge-transfer and electronic spectra. These energies, together with HOMO energy of fluorine obtained by electron-impact experiments,[9)] are shown in Fig. 1 (numerals in eV). Though LUMO energy of fluorine has not been determined as yet, 10.5 eV was evaluated from MINDO/2 by Ransil.[10)]

With these data in hand, two possible MO interactions (square-type: **A** and **B**) are examined. The energy difference of two MOs for **A** is *ca.* 16-20 eV. Taking MINDO/2 LUMO energy of fluorine as correct, the energy difference for B is slightly more than or nearly equal to that of **A**.[11)] Hence, from energy levels, **A** is preferred for electron-deficient ethylenes (C=C-W: W as an electron-withdrawing group) and **B** for electron-rich and conjugated ethylenes (C=C-D: D as an electron-donating group and C=C-C: C as a conjugative group). We propose, therefore, that the major factor in the choice of **A** is its satisfaction of "criterion of maximum overlap". Reverse interaction **B**, on the contrary, violates the above criterion (cf. the a.o.'s marked by arrow symbols in **B** are of the unfavorable symmetry type to interact). We cannot, however, exclude rhombic-type interaction **C**, whose overlappings not only partly satisfy the criterion but also, like **A**, are all in phase to cause net stabilization.[11)]

The bond distances of fluorine[12)] and C-C in ethylene,[13)] both obtained from electron diffraction study, are 1.435 (F-F) and 1.337 Å (C-C), respectively, and, thus, interaction **A** and hence the formation of complex **I** are also supported from geometrical ground.

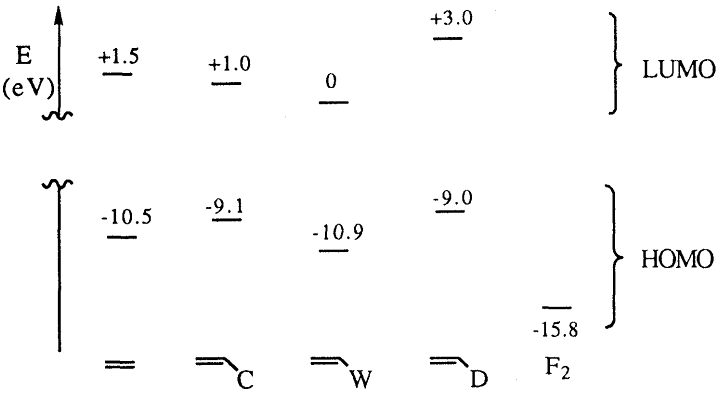


Fig. 1. Approximate Frontier Orbital Energies
(C = $CH=CH_2$, Ph, etc.; W = CHO, CN, etc.; D = R, OR, NR_2, etc.)

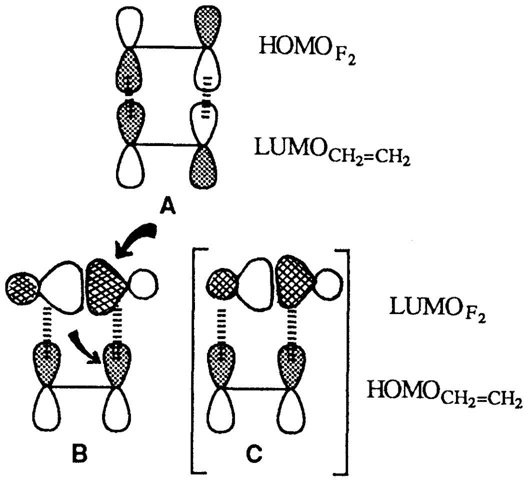
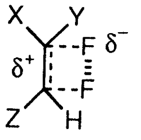


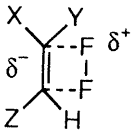
Fig 2.

Thus, as summarized in Fig. 2, the formation of **I** (interaction **A**) is supported both from HOMO-LUMO interaction and from geometrical ground. Formation of complex **I** is therefore nucleophilic in nature (cf. **A**). Merritt[6)] originally proposed complex **I** with partial charges like **I'**. It should be corrected to **I"**. When there is no possibility for **I** to convert **II**, **I** leads to the *cis*-adduct through homolytic F-F bond cleavage (bond strength of fluorine is only 37 kcal, which is the weakest one in diatomic molecules). Though this process should not proceed concertedly $(2\sigma_s +$

$2\pi_s$ cycloaddition is a forbidden reaction), both C-F bonds should be formed on the same side due to close proximity of two fluorine radicals.



I'



I''

In conclusion, a mechanism for the direct low temperature addition of molecular fluorine to ethylenes has been proposed. The mechanism not only explains the well known *syn* addition preference verified experimentally, but also predicts that this is not an electrophilic reaction[14] (at least for electron-deficient ethylenes[15]) and would be applicable to all kinds of ethylenes.

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