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## The Role of LiAlH<sub>4</sub> in the Photolysis of Benzyl Fluoride Derivatives

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Abstract: Benzyl fluoride derivatives show little reactivity under photochemical conditions, while an enhancement of conversion was observed when photoirradiation was performed in the presence of  $LiAlH_4$ .

The chemistry of the fluorine containing organic compounds is marked by special properties of the carbon-fluorine bond. Its stability depends on the structural features of the molecule and on experimental conditions. In aliphatic molecules the C-F group is more stable towards hydrolysis than other halogens bound in the like fashion. Hydrolysis of organic fluorides is assisted by acid<sup>1</sup> or by some metals; thus, benzyl fluoride readily hydrolyzes in the presence of metals, such as Al and especially Zr and Th.<sup>2</sup> It is interesting to note that hydrolysis of benzyl fluoride is much more difficult than that of benzyl chloride in alkaline or neutral media, however under acidic conditions it is much faster. Due to environmental pollution problems, the photochemistry of organic halo substituted compounds has been intensively studied. The lowest energy transition of alkyl halides involves promotion of an n electron located on the halogen atom to the  $\sigma^*$  antibonding molecular orbital. However, the high energy required for the  $n \rightarrow \sigma^*$  transition makes alkyl fluorides photostable, except in vacuum UV.<sup>3</sup>

In most of the reductions with metals, C-F bond is unreactive except when fluorine atom is adjacent to a double bond, to an aromatic ring, or to some other type of unsaturation.<sup>4</sup> In such a case it may be replaced by hydrogen atom, if the reaction is carried out in protic solvents. Metal hydrides usually do not react with saturated fluorinated molecules. Only a few examples of replacement of fluorine are recorded in the literature.<sup>5</sup>

In order to establish the photobehavior of benzyl fluoride derivatives in the presence of metal hydride, these were subjected to direct photolysis as well as to photolysis in the presence of  $LiAlH_4$ .

Eight hours irradiation of 0.01 M THF solution of 1,2-diphenyl-1-fluoroethane<sup>6</sup> at  $\lambda$ =253.7 nm resulted in 18% conversion to cis and trans stilbene, while only a slight change in conversion and products distribution was observed, when irradiation was carried out in the presence of radical inhibitor 2,6-di-t-butyl-4methylphenol, indicating that free radicals were not involved (Table).

Before the reactivity of 1,2-diphenyl-1-fluoroethane (1a) and LiAlH<sub>4</sub> under photolytic conditions could be studied, the stability of 1a in the presence of LiAlH<sub>4</sub> had to be established. Therefore, a THF solution of 1a was stirred in the presence of LiAlH<sub>4</sub> for eight hours and only 8% conversion of 1a to cis and trans stilbene



**TABLE:** Products distribution (relative yields in  $\%)^{a}$ )

reaction conditions <sup>b)</sup>	1	2	3	4	5	6	7	8
ф-СН <b>F</b> -СҢ <sub>2</sub> -ф	82	82	-	-	-	14	4	-
∲-CHF-CH <sub>2</sub> -∳ + DBPC	75	75	-	-	-	18	7	-
φ-CHF-CH <sub>2</sub> -φ + LiAlH <sub>4</sub> (no irradiation)	92	92	-	-	-	5	3	-
φ-CHF-CH₂-φ + LiAlH₄	34	34	-	-	-	23	4	39
ф-СF <sub>2</sub> -СН <sub>2</sub> -Ф	92	-	3	5	-	-	-	-
φ−CF <sub>2</sub> −CH <sub>2</sub> -φ + DBPC	89	-	4	5	2	-	-	-
$\phi$ - CF <sub>2</sub> -CH <sub>2</sub> - $\phi$ + LiAlH <sub>4</sub>	100	-	-	-	-	-	-	-
$\phi - CF_2 - CH_2 - \phi + UAIH_4$	46	19	-	-	1	9	15	10
∲-CHF-CHF-¢	99	_	-	_	-	-	1	-
$\phi$ -CHF -CHF - $\phi$ + LiAIH <sub>4</sub> (no irradiation)	100	-	-	-	-	-	-	-
∲=CHF=CHF-∳ + LIAIH₄	42	2	-	-	-	21	30	5

a) determined by GC - MS

b) substrate: 0.01 M; solvent: THF; time: 8 hours: λ=253.7 nm; DBPC: 2,6-di-t-butyl-4-methylphenol: 0.01 M; LiAIH<sub>4</sub>: 0.02 M. was observed. However, when a THF solution of 1a and LiAlH<sub>4</sub> was subjected to UV irradiation ( $\lambda$ =253.7 nm), a much higher conversion of 1a resulted and besides cis and trans stilbene 39% of 1,2-diphenylethane was formed.<sup>7</sup> The use of LiAlD<sub>4</sub> instead of LiAlH<sub>4</sub> led to the formation of 1,2-diphenyl-1-deuteroethane and 1,2-diphenyl-1,1-dideuteroethane, thus showing that hydride served as a hydrogen source.

The results obtained strongly suggest that the reduction of the carbon-fluorine group occurred in the excited state of substrate by electron transfer from  $AlH_4^{\Theta}$  to fluorine atom, thus leading to reduction product 1,2-diphenylethane. However, coordination between  $Li^{\oplus}$  as a hard acid and the excited state of 1,2-diphenyl-1-fluoroethane, followed by hydride attack, is also possible (Scheme 2).

## $\begin{array}{cccc} \phi - CH - CH_2 - \phi & hv & \left[ \phi - CH - CH_2 - \phi \right]^* \\ F & \left[ \begin{array}{c} \phi - CH - CH_2 - \phi \\ F \end{array} \right]^* \\ \phi - CH - CH_2 - \phi & \phi - CH - CH_2 - \phi \\ \phi - CH - CH_2 - \phi & \phi - CH - CH_2 - \phi \\ \phi - CH_2 - CH_2 - \phi & F^{-1} AlH_4^{\circ} \\ AlH_4^{\circ} & & & \\ \phi - CH_2 - CH_2 - \phi & + LiF + AlH_3 \end{array}$

Further, the influence of the second benzylic fluorine atom bonded on substrate reactivity is of interest and therefore, 1,1-difluoro-1,2-diphenylethane<sup>8</sup> and 1,2-difluoro-1,2-diphenylethane<sup>9</sup> were synthesized.

Irradiation of a THF solution of 1,1-difluoro-1,2-diphenylethane (1b) under the same conditions as in previous cases resulted in only 8% conversion into a mixture of cis and trans fluoro stilbene. While no reduction of C-F bond occurred. However, when irradiation was carried out in the presence of LiAlH<sub>4</sub>, a complex reaction mixture was obtained containing 46% of starting compound, 19% of 1-fluoro-1,2diphenylethane, 1% of 9-fluorophenanthrene, 9% of trans stilbene, 15% of cis stilbene and 10% of 1,2-diphenylethane. In the first step photoreduction of C-F bond by LiAlH<sub>4</sub> must occurr giving the monofluoro derivative which can be further transformed either by photoelimination of HF to cis and trans stilbene, or to 1,2-diphenylethane by photoreduction of another C - F bond with LiAlH<sub>4</sub>. Absence of cis and trans fluorostilbene indicates that photoreduction of fluorostilbenes by LiAlH<sub>4</sub> could also occurr. In the dark, 1,1-difluoro-1,2-diphenylethane is stable in the presence of LiAlH<sub>4</sub>.

Introduction of a second fluorine atom into the substrate increased its photostability, which was also the case when it was bonded to a vicinal benzylic position. Thus, eight hours irradiation of 1,2-difluoro-1,2-diphenylethane (1c) led to only 1% conversion (Table). Also, no reaction occurred between 1c and LiAlH<sub>4</sub> in the dark. On the other hand, irradiation of a THF solution of 1c in the presence of LiAlH<sub>4</sub> resulted in 58 % conversion and besides cis and trans stilbene a small amount of 1,2-diphenyl-1-fluoroethane and

## SCHEME 2

1,2-diphenylethane was also formed, thus showing that photoelimination of hydrogen fluoride and photosubstitution of fluorine atom by hydrogen atom must be the competitive processes.

On the basis of the results obtained, we can conclude that 1-fluoro-1,2-diphenylethane, 1,1-difluoro-1,2-diphenylethane and 1,2-difluoro-1,2-diphenylethane are relatively stable under 253.7 nm irradiation. In the presence of LiAlH<sub>4</sub>, photoelimination and photoreduction take place, resulting in cis and trans stilbene and 1,2-diphenylethane formation. Photoreduction probably occurrs through electron transfer from  $AlH_4^{\Theta}$  ion to fluorine atom of the photoexcited molecule, followed by hydrogen atom transfer.

## **References and Notes**

- 1 Gardner, C. J. Am. Chem. Soc. 1960, 82, 6104.
- 2 Clark, H.R.; Jones, M.M. J. Am. Chem. Soc. 1969, 91, 4302.
- 3 Gilbert, A.; Baggott, J. Essentials of Molecular Photochemistry; Blackwell Scientific Publications; Oxford, 1991; pp. 462.
- 4 Hudlicky. M. Chemistry of Organic Fluorine Compounds; 2nd Revised Edition; Ellis Horwood Limited; Chichester, 1992; pp.188.
- 5 Edgell, W.F.; Parts, L. J. Am. Chem. Soc. 1955, 77, 5515; Hauptschein, M.; Saggiomo, A.J.; Stokes, C.S. J. Am. Chem. Soc. 1956, 78, 680.
- 6 Weigert, F.J. J. Org. Chem. 1980, 45, 3476.
- 7 Typical experimental procedure: 0.1 mmol of substrate was dissolved in 9 ml of THF, 0.2 mmol of LiAlH<sub>4</sub> (1 ml of 0.2 M THF solution) was added and the reaction mixture was irradiated with 6 RPR 253.7 nm lamps for eight hours. The solution was then poured into 5 ml of water to destroy an excess of LiAlH<sub>4</sub> and aluminium was removed by complexation with 5 ml of saturated aqueous solution of potassium sodium tartrate. After extraction with 20 ml of ether:pentane (3:1), the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent evaporated under reduced pressure and the crude reaction mixture analyzed by GC-MS.
- 8 Patrick, T.B.; Scheibel, J.J.; Hall, W.E.; Lee, Y.H. J. Org. Chem. 1980, 45, 4492.
- 9 Olah, G.A.; Welch, J.T.; Vankar, Y.D.; Nojima, M.; Kerekes,; I. Olah, J.A. J. Org. Chem. 1979, 44, 3872.

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