PREPARATION OF 1-FLUOROACETYLENES IN A TESLA EXCITED DISCHARGE

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ABSTRACT

1-Fluoroacetylenes are readily prepared by means of a Tesla excited discharge in vapours of fluoro-substituted benzenes and azines. Generally the yield is low. However, the technique allows the preparation of sufficient amount for various kinds of spectroscopical investigations.

1. INTRODUCTION

1-Fluoroacetylenes ($F-C\equiv C-X$) have attracted particular interest to spectroscopy and theoretical chemistry. However, the preparation of these compounds turned out to be problematic because of their unique reactivity. Conventional methods (elimination-reactions, pyrolysis) have been restricted to the synthesis of only a few derivatives : X = $-H$, $-F$, $-Cl$, $-CF_3$, $-C_4H_9$, $-COF$ and $-Si(CH_3)_3$ (for a review cf. ref. [1]) and an adequate spectroscopical characterization could be obtained for three products only : X = $-H$, $-CF_3$, and $-Si(CH_3)_3$.

The situation changed with the observation, that such compounds can easily be obtained from a Tesla-excited discharge in vapours of fluoroacenes [2] . This method allowed the preparation and isolation of the following derivatives : X = $-H$, $-F$, $-CN$, $-C\equiv C-H$, $-C\equiv C-F$ and $-C\equiv C-CF_3$. Efforts to obtain the products X = $-Cl$, $-Br$, $-I$, $-CH_3$, $-CF_3$ have not been successful so far. On the other hand, the following unsaturated fluorocompounds were also identified : $CF_2=C=C=CF_2$, $CF_3-C\equiv C-C\equiv N$, $CF_3-C\equiv C-C\equiv C-CF_3$ and $F-C\equiv N$, the latter being available in particulary large yield by the discharge technique.

2. EXPERIMENTAL

A detailed description of the experimental conditions is given in ref. [2] together with a list of the spectroscopical data for the mentioned products.

3. RESULTS

The following products with molecular weights lower than (or equal to) the starting material were detected from a Tesla excited discharge in 1,3,5-trifluorobenzene $\underline{\underline{1}}$: HF , CHF_3 , H-C≡C-F , H-C≡C-H , H-C≡C-C≡C-F and H-C≡C-C≡C-H . An approximate yield could not be determined because of the presence of large amounts of hydrogen fluoride. The results which were obtained from the other substrates, hexafluorobenzene $\underline{\underline{2}}$, pentafluoropyridine $\underline{\underline{3}}$, pentafluorobenzonitrile $\underline{\underline{4}}$ and cyanuric fluoride $\underline{\underline{5}}$ are listed in table 1 .

Table 1

Approximate yields of low molecular weight products, (in mg) from 10 g starting material

Product	Discharge substrate			
	2	3	4	5
CF_4	30	30	30	80
F-C≡C-F	10	40	20	
$CF_2=CF_2$	100	200	500	400
F-C≡C-C≡C-F	20		5	
$CF_2=C=C=CF_2$		10	5	
$F-C≡C-C≡C-CF_3$	80			
$CF_3-C≡C-C≡C-CF_3$	10			
N≡C-C≡N			5	250
F-C≡N		500	150	400
$CF_3-C≡N$				10
F-C≡C-C≡N		10	150	
$CF_3-C≡C-C≡N$		50		

The products were identified mainly by their photoelectron and mass spectra. The presence of saturated fluorocarbons in the reaction mixture such as C_2F_6 , cyclo-C_3H_6 and cyclo-C_4H_8 in minor amounts is indicated but could not be unambiguously determined.

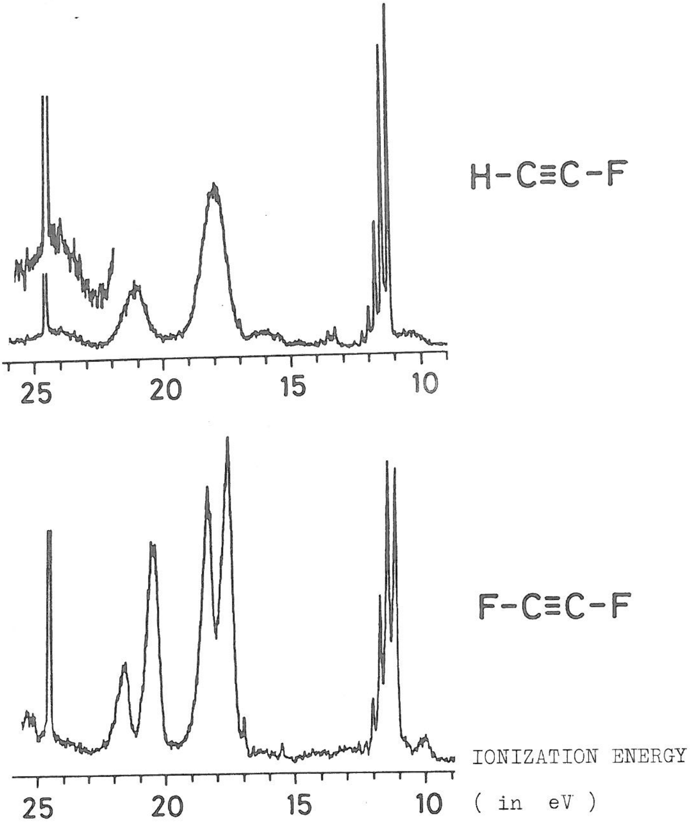
4. REMARKS

a) Some of the highly unsaturated products are very reactive and must therefore be handled with caution.

b) Although the discharge of a compound results in an enormous mixture of various products, the isolation of a pure sample is often possible by a simple bulb to bulb distillation at low pressure and under careful temperature control. Conventional gaschromatography is not well suited for the separation of these products. Usually, the decomposition of the 1-fluoroacetylenes on the column material has been observed.

c) In cases where a separation of products can not be achieved by distillation only (F-C≡N / N≡C-C≡N ; F-C≡C-C≡N / CF_3-C≡C-C≡N) it may be advantageous to change the substrate for the discharge. Using **3** as a precursor, cyanogen fluoride can be obtained which is practically uncontaminated by cyanogen. Similarily, 1-fluoro-2-cyanoacetylene is formed from **4** in the abscence of 1-cyano-3,3,3-trifluoropropyne. The latter product on the other hand is readily obtained from **3** in large excess with respect to 1-fluoro-2-cyanoacetylene.

d) Although the over-all yield of products with molecular weight lower than the starting material is rather low, this technique allows the preparation of sufficient amount of material for most spectroscopical purposes. As an illustration the 30.4 nm He(II) photoelectron spectra of H-C≡C-F and F-C≡C-F are shown in fig. 1 (The spectra are discussed in ref. [3])



e) The heat of formation $\Delta H^{0}_{f,298}$ for difluoroacetylene is estimated to be slightly negative. (MINDO/2 : + 10 kcal/Mol , MINDO/3 : - 30 kcal/Mol [4] , thermochemically, from appearance potential of $C_2F_2^+$ from C_2HF_3 : ca. - 5 kcal/Mol [5] . In other words, the neutral C_2F_2 species is thermochemically at about the same level as the hexafluorobenzene radical cation in its electronic ground state. Obviously then, difluoroacetylene can only originate as a decay-product of fragmentation processes, which take place in highly excited states of hexafluorobenzene above the ionization potential.

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