L'identification des substances est effectuée d'une part par comparaison des SM. des produits isolés de la mousse de chêne avec les spectres des produits purs enregistrés dans les mêmes conditions et les spectres de la littérature [3]. Par GC. effectuée dans des conditions standard, nous avons vérifié les temps de rétentions relatifs en utilisant comme témoin le limonène et le camphre (pour les monoterpènes) et le naphtalène (pour les sesquiterpènes et les hydrocarbures).

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29. Chemical Reactions in Electrical Discharges: Preparation of Perfluorinated Acetylenes and Nitriles

Preliminary Communication

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Summary

Several fluorinated acetylenes and nitriles have been isolated from the reaction mixture obtained from *Tesla* excited fluorinated aromatic compounds. Differences in product distributions using *Tesla* or radio frequency discharges are discussed.

Introduction. - Electrical discharges are often used to produce excited species from atoms and molecules, which subsequently can undergo interesting chemical reactions [1]. Typical textbook examples are the plasma reactions of benzene [2] [3]. This reaction proved to be very informative, because many products have been isolated, ranging from low molecular weight compounds such as acetylene, *via* condensation products, *e.g.* biphenyl, up to polymers. Obviously, the preparation of these compounds by plasma reactions is of minor interest, as they are readily obtained in much higher yields by conventional chemical methods. On the other hand, plasma chemistry might be of importance for the preparation of compounds which are difficult to obtain by other means. Being interested in perfluorinated acetylenic compounds, we therefore investigated the products formed in a *Tesla* discharge from the perfluorinated aromatic compounds **1** to **4**. In the present communication we report the isolation and identification of several fluorinated acetylenes and unsaturated nitriles.

Results. - The *table* lists products with molecular weights lower than the starting material, which are formed in an electrical discharge from hexafluorobenzene (**1**), pentafluoropyridine (**2**), pentafluorobenzonitrile (**3**) and *sym*-trifluorotriazine (**4**) under the conditions described in the experimental section. Some of the highly unsaturated products are very reactive, and must therefore be handled with caution, *i.e.* at very low temperature and/or under low pressure. The products were identified mainly by their photoelectron and mass spectra.

Table. *Approximate yields of low molecular weight products, in mg, from 10 g starting material*

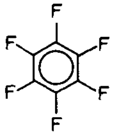
Product	Discharge substrate				Product	Discharge substrate			
	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**
CF_4	30	30	30	80	$CF_3{-}C{\equiv}C{-}C{\equiv}C{-}F$ (**7**)	80			
$F{-}C{\equiv}C{-}F$ (**5**)	10	40	20		$N{\equiv}C{-}C{\equiv}N$			< 5	250
$CF_2{=}CF_2$	100	200	500	400	$F{-}C{\equiv}N$		500	150	400
$CF_2{=}CF{-}CF_3$	30				$CF_3{-}C{\equiv}N$				10
$F{-}C{\equiv}C{-}C{\equiv}C{-}F$ (**6**)	20		< 5		$F{-}C{\equiv}C{-}C{\equiv}N$ (**8**)		10	150	
$CF_2{=}C{=}C{=}CF_2$		10	< 5		$CF_3{-}C{\equiv}C{-}C{\equiv}N$ (**9**)		50		

Remarks. - a) The substrates **1**, **2**, and **3** yield difluoroacetylene (**5**), but only with low yields. The preparation of **5** had been reported previously in [4], but because of its instability its physical and chemical properties are still not well documented. A value of 11.18 eV for the first ionization energy is deduced from the photoelectron spectrum of **5**, in perfect agreement with the theoretical prediction [5]. We did not succeed in obtaining an IR. spectrum of **5** because the highly reactive compound polymerizes rapidly at the higher pressure necessary in the spectrometer cell.

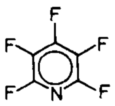
b) Two new acetylenic compounds, namely difluorobutadiyne (**6**), and tetrafluoro-1,3-pentadiyne (**7**), were isolated from the reaction mixture obtained by passing **1**, **2** or **3** through the discharge. Both are remarkably stable compared to **5**.

c) Using **2** as a precursor yields cyanogen fluoride, practically uncontaminated by cyanogen.

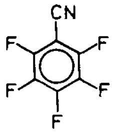
d) Whereas the diacetylenes **6** and **7** can be separated easily by high vacuum distillation at low temperature, this method fails to be convenient for the separation of the cyano substituted acetylenes **8** and **9**. Therefore it is advantageous to use **3** as starting material, because this precursor yields 1-fluoro-2-cyanoacetylene (**8**) in the absence of 1-cyano-3,3,3-trifluoropropyne (**9**).



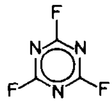
1



2



3



4

$F{-}C{\equiv}C{-}F$ **5**

$F{-}C{\equiv}C{-}C{\equiv}C{-}F$ **6**

$CF_3{-}C{\equiv}C{-}C{\equiv}C{-}F$ **7**

$F{-}C{\equiv}C{-}C{\equiv}N$ **8**

$CF_3{-}C{\equiv}C{-}C{\equiv}N$ **9**

e) Combined GC./MS. analysis of the liquid fraction of the discharge products obtained from **1**, indicated the presence of some fifty compounds in the C_6F_6 to $C_{12}F_{14}$ range. Decafluorobiphenyl was one of the major products.

f) From the products obtained by passing **1** through a 27.1 MHz radio frequency excited discharge, we could not isolate useful amounts of the fluoroacetylenes **5**, **6** or **7**. Instead, stable fluorocarbons such as C_2F_4, C_2F_6 and higher homologues together with polycondensation products of **1** were found.

These findings are in accordance with results of *Gilbert & Théorêt* [6], using a 13.56 MHz discharge, although these authors did not attempt to isolate acetylenic products from the reaction mixture.

Tentatively, we rationalize the finding, that no detectable amounts of fluoroacetylenes are formed in a radio frequency discharge from **1**, as follows. The different discharge excitation devices, namely a continuous wave radio frequency generator or a *Tesla* transformer, most probably produce different energy distributions of the plasma electrons. A radio frequency driven discharge allows the electrons to build up energy progressively [3], thus increasing the probability of low energy electron impacts with substrate molecules. Therefore, more neutral radicals will be produced compared to a *Tesla* discharge, where the high field pulses accelerate the electrons to energies above the ionization energy of the substrate within the first field oscillation. This will result in the production of predominantly ionized species. The importance of ionized molecules in plasma reactions is emphasized by results from controlled energy electron impact experiments [7], where a significant increase in product formation was observed with an electron energy exceeding the ionization energy of the hydrocarbon precursor.

Compared to a radio frequency transmitter, only low power output is attainable from a *Tesla* excitation device, which explains the low overall yield of reaction products. The influence of different parameters such as gas pressure, flow rate, discharge tube diameter, or electrical field strength on the plasma reaction is yet not well understood [1]. Certainly, higher yields of a desired product could be obtained by optimizing all these reaction parameters.

Experimental Part

The plasma reactions were performed under flowing conditions at about 0.1 Torr with a substrate flow rate of approximately 1 g/h, adjusted with a needle valve. The discharge was excited in a quartz tube (10 mm i.d., 250 mm length), using a Vacuum HF Tester Model T2 from *Edwards High Vacuum Ltd.* The spark gap of the *Tesla* transformer was set to yield maximum light emission of the plasma. Unchanged starting material and the discharge products were trapped at liquid nitrogen temperature. The low molecular weight components of the reaction mixture were separated by fractional high vacuum distillation starting at 110 K.

Mass spectral data are listed: mass in *m/e* (assignment, relative intensity to the base peak). IR. spectra are recorded in cm^{-1}. The chemical shifts of the ^{19}F-NMR. spectrum are given in ppm relative to $CFCl_3$. Ionization energies as determined by photoelectron spectroscopy (PES.) are given in eV.

Difluoroacetylene (**5**). MS.: 62 (M^+, 100); 43 (C_2F^+, 14); 31 (CF^+, 7). - PES.: $\tilde{X}$ ($^2\Pi_{\Omega,u}$) 11.18.

Difluorobutadiyne (**6**). IR. (gas): 2480, 2280, 1075. - MS.: 86 (M^+, 100); 67 (C_4F^+, 5); 55 (C_3F^+, 10); 43 (C_2F^+, 4); 36 (C_3^+, 4); 31 (CF^+, 11). - PES.: $\tilde{X}$($^2\Pi_{\Omega,g}$) 10.05; $\tilde{A}$ ($^2\Pi_{\Omega,u}$) 12.68.

Tetrafluoro-1,3-pentadiyne (**7**). IR. (gas): 2340, 1374, 1234, 1210, 1175, 895, 718. - ^{19}F-NMR. ($CDCl_3/CFCl_3$, $-30°$): -195 (*s*, 1 F); -50 (*s*, 3 F). - MS.: 136 (M^+, 100); 117 ($C_5F_3^+$, 80); 98 ($C_5F_2^+$, 7); 93 ($C_3F_3^+$, 2); 79 (C_5F^+, 3); 74 ($C_3F_2^+$, 2); 69 (CF_3^+, 8); 67 (C_4F^+, 2); 31 (CF^+, 6). - PES.: $\tilde{X}$ (^2E) 10.58; $\tilde{A}$ (^2E) 13.08.

1-Fluoro-2-cyanoacetylene (**8**). IR. (gas): 2590, 2360, 2240, 1305, 1290, 955, 945, 755, 742, 478. - MS.: 69 (M^+, 100); 50 (C_3N^+, 5); 35 (C_2N^+, 4); 31 (CF^+, 9); 26 (CN^+, 1); 24 (C_2^+, 1). - PES.: $\tilde{X}$ ($^2\Pi_\Omega$) 11.51; $\tilde{A}$ ($^2E^+$) 13.50; $\tilde{B}$ ($^2\Pi_\Omega$) 14.01.

1-Cyano-3,3,3-trifluoropropyne (**9**). MS.: 119 (M^+, 100), 100 ($C_4F_2N^+$, 90); 88 ($C_3F_2N^+$, 19); 86 ($C_4F_2^+$, 6); 76 ($C_2F_2N^+$, 3); 74 ($C_3F_2^+$, 7); 69 (CF_3^+, 40); 55 (C_3F^+, 4); 50 (CF_2^+, 11); 31 (CF^+, 20). - PES.: $\tilde{X}$ (^2E) 12.00; $\tilde{A}$ ($^2A_1$) 13.89; $\tilde{B}$ (^2E) 14.44.

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