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CHLOROFLUOROACETYLENE AND BROMOFLUOROACETYLENE BY GAS PHASE DEHALOGENATION OF 1,1-DIFLUOROETHYLENES

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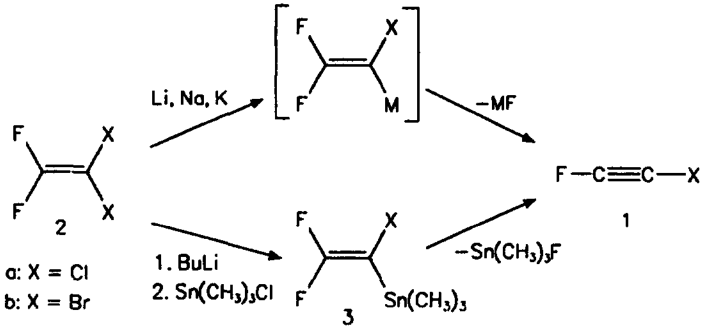
Summary: Chlorofluoroacetylene and bromofluoroacetylene have been prepared by dehalogenation of dichlorodifluoroethylene and dibromodifluoroethylene, respectively. The products of the direct dehalogenation with alkali metals as well as of the pyrolysis of trimethylstannyl compounds as "stabilized carbenoids" have been isolated in Ar matrices.

Chlorofluoroacetylene **1a**[1] and bromofluoroacetylene **1b**[2] are reactive acetylenes which can be trapped at liquid nitrogen temperature but readily decompose at higher temperatures and explode in the presence of traces of oxygen. The acetylenes **1** are prepared by dehydrohalogenation of dichlorofluoroethylene and dibromofluoroethylene, respectively, with KOH in the gas phase at 125 - 150°C[3]. Microwave spectra have been reported for **1a**[1] and **b**[2], in addition IR and ^{19}F-NMR data for **1a**[3]. During our studies of carbenoid decomposition we found an alternative procedure to prepare **1a** and **b** starting from 1,1-dichloro-2,2-difluoroethylene **2a** or 1,1-dibromo-2,2-difluoroethylene **2b** (Scheme 1).



Scheme 1

When the ethylenes **2** are treated with n-butyllithium and trimethylstannyl chloride at -95°C, α-chloro-α-trimethylstannyldifluoroethylene **3a** and α-bromo-α-trimethylstannyldifluoroethylene **3b** are obtained in 40 - 45% yield after distillation.[4] The stannyl compounds **3** have been characterized by IR, NMR and MS spectroscopy[4] and can be stored at -40°C for several months but decompose slowly at room temperature. To investigate the route of the thermal decomposition of **3** (α-elimination to give difluorovinylidene and difluoroacetylene vs. β-elimination to give acetylenes **1**) flash vacuum pyrolysis (FVP) in combination with matrix isolation was used.[5] The pyrolysis products have been characterized by IR spectroscopy. In addition, pyrolyses on a preparative scale and subsequent collection of the products at 77 K have been carried out.

FVP of **3a** at 800°C and trapping the products in Ar at 10 K gave chlorofluoroacetylene **1a** (2325.7 (m), 1201.9 (w) cm^{-1}), trimethyltinfluoride (775.7 (m) 575.1 (s), 548.6 (m) cm^{-1}) and small amounts of methane (1304 cm^{-1}) and tetramethyltin (1132, 1035, 728, 532 cm^{-1}). The IR absorptions of **1a** at 2325.7 and 1201.9 cm^{-1} are assigned to the C≡C stretching vibration and the asym. C-X (mainly C-F) stretching vibration and are close to the reported[3] gas phase absorptions at 2315, 1205 and 1194 cm^{-1}. The other products have been identified by comparison with authentic matrix isolated material. Small amounts of **1a** have also been obtained by passing **3a** over solid methyllithium[6] at 10^{-3} Torr and room temperature. Although the reaction of **3a** was complete under these conditions and large amounts of tetramethyltin were formed, the yield of **1a** was small, presumably due to secondary reactions of **3a** and methyllithium.

FVP of **3b** at 800°C gave bromofluoroacetylene **1b** (2370.5 (m), 2294.5 (m), 1172.0 (s) cm^{-1}) and trimethyltinfluoride. The splitting of the C≡C stretching mode of **1b** into two components at 2370.5 and 2294.5 cm^{-1} can be explained by Fermi resonance. The corrected C≡C stretching mode at approximately 2330 cm^{-1} is close to the first overtone of the asymmetric C-X stretching mode at 2 x 1172.0 cm^{-1}. Other products of the pyrolysis are trimethyltinbromide (767.5 (s), 530.8 (m) cm^{-1}) fluoroacetylene (2236.0 cm^{-1}), 1-bromo-2,2-difluoroethylene (3120.2, 1741.8, 1733.6, 1313.7, 1170.5, 957.0) and methane (1303.6 cm^{-1}). The minor products are presumably formed by radical reactions.

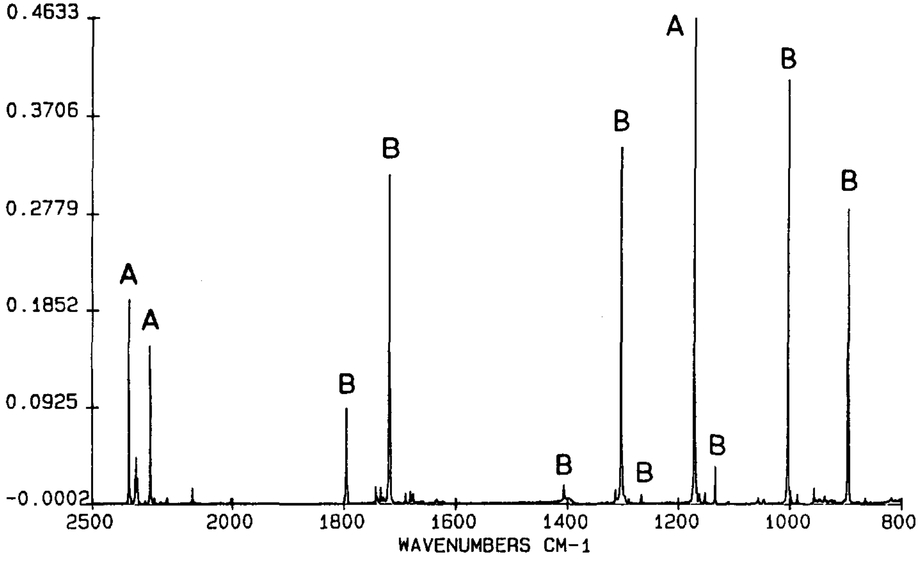


Fig. 1. IR spectrum of the products of the reaction of ethylene **2b** and Li vapour, matrix isolated in Ar at 10 K. A: bands assigned to **1b**, B: starting material **2b**. The weak absorption at 2344 cm^{-1} is caused by CO_2 from the surface contamination of Li metall.

Acetylenes **1** can also be prepared by the reaction of difluoroethylenes **2** with alkali metals in the gas phase at temperatures between 300 and 550°C. Li, Na and K were evaporated in a quartz tube at 550, 480 and 370°C, respectively, and in the gas phase mixed with ethylenes **2**. A second oven allowed to

Table 1. Calculated and experimental frequencies for the C≡C stretching mode of several halogenated acetylenes (frequencies in cm^{-1})

Acetylene	MNDO[a]	STO-3G[b]	Exper.
H-C≡C-H	1957	2002	1971[c]
H-C≡C-F	2270	2227	2255[d]
H-C≡C-Cl	2090	2154	2110[d]
H-C≡C-Br	2072	2081	2085[d]
F-C≡C-Cl	2348	2358	2315[e]
F-C≡C-Br	2331	2339	2330[f]
Cl-C≡C-Br	2236	2271	2223[g]
Br-C≡C-Br	2165	2030	2185[g]

[a] scaling factor 0.905, [b] scaling factor 0.802, [c] Ref. 9, [d] Ref. 10, [e] Ref. 3, [f] this work, [g] Ref. 11

heat the gas mixture up to 650°C. Under these conditions **2a** gave only low yields of **1a** even at the highest temperatures using Li as the most reactive metal.

As expected, 1,1-dibromo-2,2-difluoroethylene **2b** shows a much higher reactivity towards alkali metals. Treatment of **2b** with Li vapour at 350 - 400°C gave acetylene **1b** as the major product, and only trace amounts of fluoroacetylene and 1-bromo-2,2-difluoroethylene were formed (Fig. 1). Thus the reaction of **2b** with Li is a highly efficient source of **1b**.

To verify the assignment of observed IR data to **1b** we calculated C≡C stretching vibrations for several halogenated acetylenes using the semiempirical MNDO method[7] and ab initio calculations with the STO-3G minimal basis set[8] (Tab. 1). The calculated stretching frequencies were scaled with factors to give the best fit between calculation and experiment (0.905 for MNDO and 0.802 for STO-3G). For **1b** the experimental frequency at 2330 cm^{-1} (approximate fundamental vibration if the Fermi resonance is taken into account) is in good agreement with the MNDO (2331 ± 7 cm^{-1}) and ab initio (2339 ± 25 cm^{-1}) calculations.

The pyrolysis of the stannyl compounds **3** as well as the dehalogenation of ethylenes **2** gives acetylenes **1** as products of β-elimination. Minor products are formed by radical reactions, compounds formed by α-elimination have not been detected.

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4 **3a**: Bp_1 38 - 41°C; $n^D(20)$ 1.4524; MS (70 eV) 261.9452 (M^+, calc. 261.9380); ^1H-NMR ($CDCl_3$) δ 0.35 (s, 9 H, $J_{^{119,117}Sn\text{-}H}$ = 57 Hz); ^{13}C-NMR ($CDCl_3$) δ -7.44 (s), 88.07 (m), 159.47 (dd, $J_{C\text{-}F}$ = 272.9 Hz, $J_{C\text{-}F}$ = 312.4 Hz); ^{19}F-NMR ($CHCl_3$) δ -72.2 (d, $J_{F\text{-}F}$ = 39.6 Hz), -87.1 (d, $J_{F\text{-}F}$ = 39.6 Hz); IR (Ar, 10 K) 3002 (w), 2939 (w), 1697 (vs), 1251 (s), 1202 (w), 1161 (w), 989 (s), 913 (m), 780 (s), 728 (m), 722 (m), 581 (w), 547 (m), 522 (w) cm^{-1}.
3b: $Bp_{0.5}$ 28 - 30°C; MS (70 eV) 305.8950 (M^+, calc. 305.8853); ^1H-NMR ($CDCl_3$) δ 0.35 (s, 9 H, $J_{^{119,117}Sn\text{-}H}$ = 55.9 Hz); ^{13}C-NMR ($CDCl_3$) δ -7.44 (s), 69.92 (dd, $J_{C\text{-}F}$ = 75.53 Hz, $J_{C\text{-}F}$ = 10.57 Hz), 156.88 (dd, $J_{C\text{-}F}$ = 275.85 Hz, $J_{C\text{-}F}$ = 309.27 Hz); ^{19}F-NMR ($CDCl_3$) δ -65.6 (d, $J_{F\text{-}F}$ = 39.6 Hz), -79.7 (d, $J_{F\text{-}F}$ = 39.6 Hz); IR (Ar, 10 K) 3001.1 (w), 2970.3 (w), 2936.5 (w), 1725.0 (s), 1721.6 (m), 1679.2 (vs), 1238.0 (vs), 1200.4 (w), 982.0 (s), 857.2 (m), 779.5(s, br), 727.5 (w), 720.7 (w), 546.7 (m), 543.3 (m) cm^{-1}.

5 FVP was carried out using quartz tubes (4 mm i. d.) heated by Nichrome wires inside the high vacuum system. The length of the heating zone was 8 - 10 cm. IR spectra were recorded on a Bruker IFS66 (resolution 0.5 cm^{-1}, range 4000 - 500 cm^{-1}) or a Perkin Elmer PE580 (resolution 2 cm^{-1}, range 4000 - 400 cm^{-1}). For a description of the matrix expriments see: [a]W. W. Sander *J. Org. Chem.* **54**, 333 (1989); [b]W. W. Sander *J. Org. Chem.* **53**, 121 (1988).

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