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SHORT COMMUNICATION

A Simple Synthesis for Carbon-13 Enriched Fluorochloromethanes and Fluoromethanes.

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With the recently proposed role of "Freon" compounds in the depletion of ozone in the stratosphere [1], there has been vigorously renewed interest in the fluorochloromethane molecules. Two gas-phase photoionization studies of $CFCl_3$, CF_2Cl_2 and CF_3Cl have appeared recently[2,3]. In this laboratory, we have performed argon resonance photoionization of these molecules followed by trapping of the product ions in solid argon for infrared spectroscopic examination [4]. These studies required carbon-13 isotopic substitution to confirm the vibrational assignments to the molecular ions in solid argon. In view of the current interest in "Freon" compounds, we report here a simple, quantitative vacuum line method for synthesizing millimole quantities of carbon-13 enriched $CFCl_3$, CF_2Cl_2 and CF_3Cl from $^{13}CCl_4$; we also report the synthesis of C-13 enriched CHF_3, CHF_2Cl and $CHFCl_2$ from $^{13}CHCl_3$, and of CH_2F_2 and CH_2FCl from $^{13}CH_2Cl_2$.

In order to conserve the expensive carbon-13 enriched starting material, it was desired to transfer one millimole of precursor under vacuum to a fluorinating medium of the proper strength to exchange only the desired number of chlorine atoms, and then distill the product from the reaction mixture. Hudlicky [5] has noted the following order of reagent fluorinating power:

$$SbF_3 < (SbF_3 + SbCl_3) < (SbF_3 + SbCl_5) < SbF_3Cl_2 < SbF_5$$

The degree of fluorine substitution was controlled by reagent fluorinating power and to a lesser extent by reaction time and temperature.

Experimental Section

The reactions were performed on a vacuum line (evacuated to 10 torr) made with ¼" stainless steel "swagelok" fittings, bellows valves (Nupro), and a vacuum gauge (Ashcroft). Pyrex reaction vessel a 10-cm infrared gas cell, and storage vessels were attached to the vacuum line by 14/35 standard taper joints sealed with silicone vacuum grease (Dow-Corning).

Four different fluorinating media were prepared:

(1) 20 gm of $FSO_3H \cdot SbF_5$ (Magic Acid, Aldrich) in a 50 ml pyrex vessel with a teflon plug stopcock (Kontes).

(2) Approximately 4 gm of solid SbF_3 (Fisher Scientific) and 4 gm of liquid $SbCl_5$ (Fisher Scientific) in a similar pyrex vessel.

(3) 4 gm of solid SbF_3 and 5 drops of liquid $SbCl_5$ in a pyrex vessel.

(4) 5 gm of HgF_2, prepared by the reaction of F_2 with $HgCl_2$, in a valved 12-mm stainless steel tube.

The fluorinating agents were placed in these vessels in a glove bag under argon, and the vessels were immediately evacuated.

$\underline{^{13}CF_3Cl}$. One millimole of CCl_4 was condensed, outgassed, transferred under vacuum and condensed on reagent (1). After warming the mixture to 25°C, bubbling was observed on the CCl_4-"Magic Acid" interface. The mixture was gently agitated intermittently for 2 hrs and then cooled to -127°C; the product was distilled at this temperature into a gas cell for obtaining the infrared spectrum which showed almost complete conversion to CF_3Cl[6]. One millimole of $^{13}CCl_4$ (90% ^{13}C, Merck Sharpe and Dohme, Canada) was condensed with reagent (1); infrared spectra recorded at two hr intervals showed that 7 hrs of reaction at 25°C were required for quantitative conversion to $^{13}CF_3Cl$. The product was distilled from the reaction mixture at -127°C and stored in a pyrex vessel.

$\underline{^{13}CHF_3}$. The above procedure was repeated with $CHCl_3$ and complete fluorination was obtained after 4 hrs of reaction. One millimole of $^{13}CHCl_3$ (Merck Sharpe and Dohme, Canada) was condensed with reagent (1) and reacted for 4 hrs at 25°C. The $^{13}CHF_3$ yield was quantitative as verified from pressure-volume measurements and infrared spectra. Although pure SbF_5 was not used in the present reactions, it is expected that neat SbF_5 would produce similar results to the "Magic Acid" used here.

$\underline{^{13}CF_2Cl_2}$. One millimole of CCl_4 was condensed with reagent (2) and reacted for 2 hrs at 40°C. The volatile product was determined by infrared analysis to be essentially all CF_2Cl_2. Pure $^{13}CF_2Cl_2$ could have been prepared with this reagent; however, further syntheses were performed with reagent (3). Carbon tetrachloride failed to react with pure SbF_3 even at 160°C for 2 hrs. Five drops of liquid $SbCl_5$ were added to the SbF_3 vessel under an argon atmosphere, and after

2 hrs of reaction with CCl_4 at $25^{\circ}C$, a substantial yield of both $CFCl_3$ and CF_2Cl_2 was found. One millimole of $^{13}CCl_4$ was reacted with reagent (3) at $25^{\circ}C$ and the reaction was monitored by infrared analysis Two days were required for quantitative conversion to $^{13}CF_2Cl_2$.

$^{13}CFCl_3$. One millimole of $^{13}CCl_4$ was condensed with reagent (3), and the mixture was maintained at $0^{\circ}C$ to enhance the yield of $^{13}CFC_2Cl_2$ After 1.5 hrs of reaction, the product distilled off at $0^{\circ}C$ was almost completely $^{13}CFCl_3$. A small amount of $^{13}CF_2Cl_2$ was removed from the product by a preparative gas chromatograph using an Apiezon-L column maintained at $25^{\circ}C$. It is important to monitor the progress of the fluorine substitution reaction by infrared analysis to control the desired yield of product.

$^{13}CHFCl_2$. The reagent (3) was reacted with one millimole of $^{13}CHCl_3$ at $0^{\circ}C$ and the volatile product was analysed at one hr intervals. After 3 hrs, the major product was $^{13}CHFCl_2$. The preparative gas chromatograph with an Apiezon-L column was used to remove $^{13}CHF_2Cl$ and unreacted $^{13}CHCl_3$.

$^{13}CHF_2Cl$. One millimole of $CHCl_3$ was reacted with reagent (2) at 6 for 2 hrs; the volatile product was approximately 60% CHF_3 and 40% CHF_2Cl by infrared analysis. The reaction was repeated at $0^{\circ}C$ for 2 hrs and the volatile product was approximately 20% CHF_3, 40% CHF_2 20% $CHFCl_2$ with 20% unreacted $CHCl_3$. One millimole of $^{13}CHCl_3$ was transferred onto reagent (2) and the medium was warmed to $40^{\circ}C$; the volatile product was distilled off at $-90^{\circ}C$ at half-hour intervals.

Six fractions were collected, and 80% of the original $^{13}CHCl_3$ was converted to $^{13}CHF_2Cl$ by this procedure.

$^{13}CH_2F_2$ and $^{13}CH_2FCl$. Methylene chloride was condensed with reagents (1), (2) and (3). In each case, a non-volatile presumably polymeric product was formed. A new reagent prepared from pure SbF_3 and Cl_2 gas, which yields SbF_3Cl_2, was reacted with CH_2Cl_2 ($Cl_2/CH_2Cl_2 = 2/1$); after 2 days of reaction at 25°C, some conversion to CH_2F_2 and CH_2FCl, as well as reagent loss due to side reaction, was observed. CH_2Cl_2 was then condensed on solid HgF_2, reagent (4), and after 1 hr of reaction at 240°C, the volatile product was estimated to be 75% CH_2F_2 and 25% CH_2FCl from infrared spectra. Two millimoles of $^{13}CH_2Cl_2$ were added to the HgF_2 reagent and heated to 230°C, and the volatile product was distilled off at -75°C every half-hour; a total of 5 fractions were collected. The mixture of $^{13}CH_2F_2$ and $^{13}CH_2FCl$ was separated on a preparative gas chromatograph using a room temperature tricresyl phosphate column. Each fraction was then purified by two additional passes through the chromatograph, and approximately 1.0 millimoles of $^{13}CH_2F_2$ and 0.5 millimoles of $^{13}CH_2FCl$ were recovered. It is important to monitor the progress of this reaction with infrared spectra so that reagent temperature and reaction time can be adjusted to give the desired yield of each product.

The synthetic methods described above work equally well for deuterium and carbon-13 substituted compounds. Fluoroform-d and methylene fluoride-d_2 were synthesized from $CDCl_3$ and CD_2Cl_2, respectively. This method, however is limited to fluorine substitution for chlorine (or bromine) in the available carbon-13 or deuterium labeled compound. For molecules like $^{13}CF_3Br$, a more involved synthesis is required [7], since $^{13}CBr_4$ is difficult to prepare quantitatively from the elements.

Warning. In an attempt to synthesize $CHFI_2$, approximately 1 cc of s-iodoform was mixed with an equal volume of 10 year old mercurous fluid (Hg_2F_2), placed in a glass finger and evacuated. Immediately upon heating with a hot air gun, the mixture detonated. Great caution should be exercised with reactions of this type.

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