teresting to note the considerable shortening of the cd distance in going from **3** to **16** (cd = 3.21 Å, MMX) and **16a** (cd = 3.19 Å, MMX).[15]

The described chemistry supports epoxide opening[1c] as a triggering mechanism for the action of dynemicin A, paves the way for the total synthesis of this natural product, and suggests the potential of these and related systems as novel DNA-cleaving molecules and anticancer agents.

**Acknowledgment.** We thank Dr. Raj Chadha, University of California, San Diego, for the X-ray crystallographic analysis of compounds **2** and **3** and Drs. Dee H. Huang and Gary Siuzdak, Research Institute of Scripps Clinic, for their NMR and mass spectroscopic assistance, respectively. This work was financially supported by the National Institutes of Health and the Research Institute of Scripps Clinic.

**Supplementary Material Available:** A listing of $R_f$, $^1H$ and $^{13}C$ NMR, and mass spectral data for compounds **2**, **3**, **9–11**, **13–15**, **18**, and **18a**, X-ray crystallographic data for compounds **2** and **3**, and NMR spectra of compounds **2**, **3**, **8–11**, **13–15**, **18**, and **18a** (41 pages). Ordering information is given on any current masthead page.

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(14) The calculated distance between these acetylenic carbons in dynemicin A was found to be 3.40 Å. See: Semmelhack, M. F.; Gallagher, J.; Cohen, D. *Tetrahedron Lett.* **1990**, *31*, 1521–1522.

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# Chloromethyl Cations in Cryogenic $SbF_5$ Matrices and the Generation of Carbocations from Hydrocarbons

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*Received June 14, 1990*

Trichloromethyl cation and other metastable halonium ions have previously been produced and spectroscopically characterized as matrix photoionization and photolysis products of halomethanes.[1-3] Recently, Olah et al.[4,5] succeeded in preparing trihalomethyl cations under long-lived stable ion conditions in superacid solutions at −78 °C. In this communication we report that chloromethyl cations can also be prepared in cryogenic antimony pentafluoride matrices from carbon tetrachloride, chloroform, and methylene chloride, respectively, by the application of the same technique used in the preparation and spectroscopic identification of carbocations.[6] In addition, the trichloromethyl cation has been shown to be an excellent reagent for the generation of carbocations from corresponding hydrocarbons in the $SbF_5$ matrix.

Codeposition of the above named chloromethanes with $SbF_5$ at 77 K on a CsI window and subsequent warming to 150 K produced the corresponding ions, i.e., $CCl_3^+$, $CHCl_2^+$, and $(ClCH_2)_2Cl^+$, as ion pairs with $Sb_2F_{10}Cl^-$ which were identified by their IR spectra (Table I). The spectral assignments can be supported by the following arguments.

**Table I.** Infrared Frequencies of Chloromethyl Cations

| starting material | cation | IR data, cm$^{-1}$ | |
|---|---|---|---|
| | | lit. | this work |
| $CCl_4$ | $CCl_3^+$ | 1035[a] | 1040 (vs) |
| $CHCl_3$ | $CHCl_2^+$ | 3033[b] | |
| | | 1291 | 1290 (s) |
| | | 1045 | 1045 (vs) |
| | | 845 | 850 (s) |
| $CH_2Cl_2$ | $(ClCH_2)_2Cl^+$ | | 3070 (m), 3068 (m), 2980 (m), 1233 (w), 1030 (s), 870 (vs), 796 (s), 780 (s) |

[a] Reference 7. [b] Reference 8.

**$CCl_3^+$.** This ion was first observed by Jacox[7] in the argon matrix at 14 K among the products of ultraviolet and microwave radiation decomposition of chloroform.[8a] They assigned the strong absorption band at 1037 cm$^{-1}$ to the asymmetrical C–Cl stretching vibration. This relatively high frequency is indicative of a partial double-bond character of this bond as predicted from the canonic resonance structures:

$$Cl_2C^+{-}Cl \leftrightarrow Cl_2C{=}Cl^+$$

In the solid $SbF_5$ matrix this band appeared at 1040 cm$^{-1}$ and was also present at 1045 cm$^{-1}$ in the vibrational spectrum of $CHCl_2^+$ (see Table I). Its appearance at 150 K was accompanied by the disappearance of the absorption at 785 cm$^{-1}$ characteristic for the C–Cl stretching vibration in carbon tetrachloride.

**$CHCl_2^+$.** An extensive list of experimental frequencies for this ion is available,[8] but attempts to prepare it in superacid from chloroform have so far been unsuccessful. However, we succeeded in generating it in the cryogenic matrix. At 150 K, signals of the codeposited chloroform in $SbF_5$ changed, with the appearance of three strong new signals characteristic of the $CHCl_2^+$ ion (Table I). The scaled theoretical vibrational frequencies[8b] for the three observed bands (in cm$^{-1}$) are 1365 (H–C–Cl in-plane bend), 1013 (C–Cl asymmetric stretch), and 818 (C–Cl symmetric stretch). When the matrix was warmed to 200 K, the original signals disappeared and new signals at 3020, 1375, 1150, and 1113 cm$^{-1}$ became visible. By comparison with the known data[9] (3036, 1373, 1152, and 1117 cm$^{-1}$), we believe that these signals belong to $CHF_3$ formed by halogen exchange and partial diffusion from the matrix material. This exchange reaction is likely to be responsible for the failure to produce this ion in superacids.

**$(ClCH_2)_2Cl^+$.** In the matrix experiment with $CH_2Cl_2$, a complicated spectrum was obtained at 150 K which because of its complexity cannot belong to the $CHCl_2^+$ ion. Since in the analogous reaction with $SbF_5$ in liquid $SO_2$ the bis(chloromethyl)chloronium ion (**1**) was formed,[5] we believe that the observed spectrum belongs to this ion. When the matrix was warmed to 200 K, signals belonging to $CH_2F_2$ appeared which must have been formed by an exchange reaction similar to the one described above. In this case the chemical ionization of $CH_2Cl_2$ differs from the photoionization in the argon matrix where $CHCl_2^+$ is formed. The chemical ionization probably first produces the unstable $CH_2Cl^+$ ion, which reacts immediately with the unreacted methylene chloride, forming the chloronium ion (**1**).

**Generation of Carbocations.** At 75 K, a thin film of $SbF_5$ was deposited on the CsI window by using the already described apparatus,[6a] followed by the concomitant deposition of $SbF_5$, $CCl_4$, and the respective hydrocarbon. If the matrix is allowed to warm slowly to about 150 K, the progress of reactions 1 and 2 can be followed spectroscopically. In the isodesmic reaction (2), the first-formed trichloromethyl cation is consumed by the hydrocarbon as the equilibrium is shifted in favor of the thermodynamically more stable carbocation. A demonstration of this

$$CCl_4 + SbF_5 = CCl_3^+ + SbClF_5^- \qquad (1)$$

$$CCl_3^+ + RH = R^+ + CHCl_3 \qquad (2)$$

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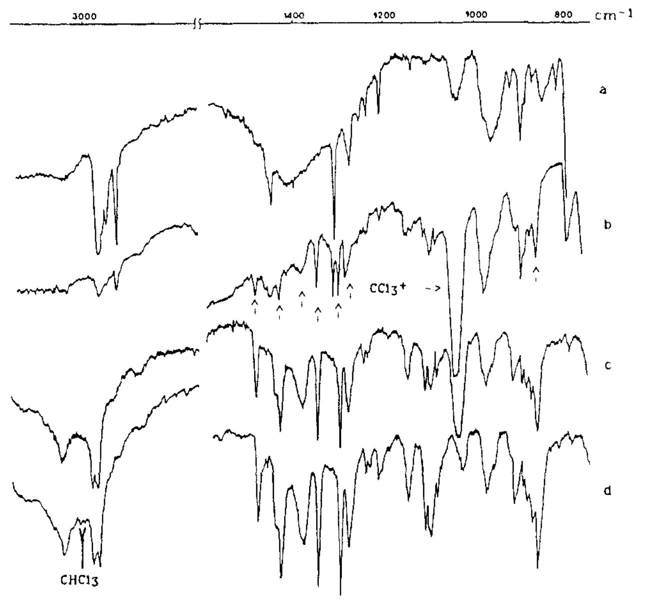
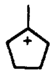
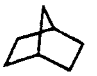
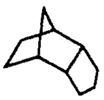
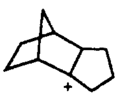
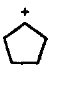
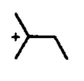


Figure 1. The reaction of norbornane with $CCl_3^+$ in the $SbF_5/CCl_4$ matrix: (a) starting material; (b—d) after successive warming from 77 to 150 K (the signals of 2-norbornyl cation are labeled with arrows).

Table II. Experimental Infrared Frequencies of Carbocations Generated in the Matrix Experiment at 150 K

| precursor | ion | freq, cm$^{-1}$ |
|---|---|---|
|  |  | 2910 s, 2850 s, 2750 s, 1456 m, 1400 m, 1310 vs,<br>1270 vs, 1210 m, 1150 w, 1105 w, 980 m,<br>910 m, 900 w |
|  |  | 3100 m, 2970 m, 2940 m, 1480 s, 1430 vs, 1380 s,<br>1350 vs, 1300 vs, 1280 s, 1245 w, 1235 vw,<br>1225 m, 1150 m, 1125 s, 1100 s, 1090 m,<br>1035 m, 980 m, 965 w, 920 w, 865 s |
|  |  | 2890 s, 2840 w, 1480 s, 1450 m, 1435 vw, 1350 m, 1320 m, 1255 m, 1190 w, 1170 s,<br>1150 w, 1115 vw, 1100 w, 1080 s, 1070 s,<br>1005 s, 973 s, 900 s |
|  |  | 2950 m, 1485 s, 1455 s, 1215 s, 1150 m, 1105 s,<br>980 s, 915 s |
|  |  | 2955 m, 2880 w, 2770 w, 1460 s, 1380 m, 1360 m, 1310 m, 1265 m, 1215 m, 1150 vs,<br>1100 s, 980 vs, 915 vs, 900 s |
|  |  | 2830 m, 1465 m, 1300 s, 1280 w, 1270 w, 1100 m, 1085 w, 1040 vs, 980 s, 910 w, 900 m |

method is shown in Figure 1 for the reaction of norbornane with $CCl_3^+$. The characteristic strong absorption band at 1040 cm$^{-1}$ assigned to the C–Cl stretching vibration of $CCl_3^+$ gradually diminishes in intensity with the simultaneous appearance of bands characteristic for the 2-norbornyl cation.[6b] Also, in the C–H stretching region two new weak bands ascribed to chloroform could be observed. In this manner carbocations listed in Table II have been prepared and characterized by (a) quenching with water to the corresponding alcohols and (b) their IR spectra, which were identical with the ones obtained[6] from (cyclo)alkyl chlorides as precursors. The IR spectra of so-prepared carbocations were in most cases of a better quality than when alkyl chlorides were used as starting material.

In the experiment with *endo*-trimethylenenorbornane, the formation of a tertiary carbocation could be observed which was not the 1-adamantyl cation as the most stable of all $C_{10}H_{15}^+$ ions. Recently, Olah, Schleyer, and their collaborators[10,11] have shown that the first intermediate generated from trimethylenenorbornane at −60 °C is the 5,6-trimethylene-4-norbornyl cation. Since in the Schleyer–Donaldson mechanism[12] of this rearrangement all intermediary ions are higher in energy, it is not surprising that also in the matrix the reaction is confined to the formation of the first unrearranged ion.

These experiments also shed some light on the mechanism of cationic rearrangements which were observed in the solid state below 150 K.[13] Since reaction 2 can take place by only an *inter*molecular hydride abstraction, it is likely that in cases where *intra*molecular hydride shifts are precluded by symmetry or other reasons, these rearrangements follow the *inter*molecular path.

**Acknowledgment**. This work was supported by the Research Council of Croatia and the National Science Foundation (U.S.), Grant No. 841.

**Supplementary Material Available**: IR spectra of $CCl_3^+$ and starting $CCl_4$, of $CHCl_2^+$ and starting $CHCl_3$, and of $(ClCH_2)_2Cl^+$ and starting $CH_2Cl_2$, all recorded between 77 and 150 K (3 pages). Ordering information is given on any current masthead page.

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## Novel Noninvasive in Situ Probe of Protein Structure and Dynamics

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*Received May 21, 1990*

7-Azatryptophan is an ideal noninvasive in situ probe of protein structure and dynamics and provides an alternative to the use of tryptophan. 7-Azatryptophan affords a single-exponential fluorescence decay in aqueous solution, unlike tryptophan. Its absorption and fluorescence spectra are distinguishable from those of tryptophan. Its fluorescence spectrum and lifetime are sensitive to the environment. It can be used in peptide synthesis, and it can be incorporated into bacterial protein. These facts render 7-azatryptophan a unique probe that has the potential for widespread use.

Tryptophan has been the most common optical probe of protein structure and dynamics.[1,2] There are, however, two major problems attendant to its use in fluorescence measurements. First, since it is a naturally occurring amino acid, there are often several tryptophans whose emission must be distinguished in a protein molecule. Second, the fluorescence decay of tryptophan itself in aqueous solution is nonexponential.[3-6] It is clearly desirable to

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