Preparation of Chloromethane-^{35}Cl and Tetrachloromethane-$^{35}Cl_4$ *

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In connection with certain Raman studies by Bernstein *et al.* [1] it became necessary to synthesize the title compounds with a chlorine-35 abundance of 96 % instead of the normal 75.5%. We planned to prepare chloromethane-^{35}Cl first and then to chlorinate it to tetrachloromethane-$^{35}Cl_4$. Deuterated methyl fluoride, chloride and bromide were successfully prepared first by Edgell and Parts [2] and later by us [3] from methyl tosylate and potassium fluoride, calcium chloride and calcium bromide respectively. Because chlorine-35 is available only as sodium chloride-35 and is difficult to convert to the calcium salt, we chose to prepare methyl chloride-35 from methyl tosylate and aluminium chloride-35, after having tried unsuccessfully to obtain the desired chloride from methyl tosylate and sodium or silver chloride. Aluminium chloride is easily prepared by heating silver chloride and finely divided aluminium [4]. Methyl chloride-35 was thus obtained in 82% yield on a decimole scale.

The only practical laboratory method of preparing ordinary carbon tetrachloride is by exhaustive photochlorination of methane or of partly chlorinated methanes. Carbon-^{14}C tetrachloride was thus prepared by Beamer [5]. An inconvenient feature of this procedure and indeed of all methods based on the chlorination of methane (or methyl chloride) is the large amount of hydrogen chloride resulting from the substitution reaction. On the one to two millimole scale (0.150 to 0.300 g) employed by Beamer, the inconvenience is minimal but on a decimole level the use of a very large reaction flask is mandatory to maintain the pressure in the system at or slightly below one atmosphere. In the present work this problem was circumvented by conducting the chlorination in the presence of a small amount of water which dissolves the hydrogen chloride as fast as it is formed. Chlorine-35 was later recovered from the aqueous solution as silver chloride-35 which was reused in the preparation of more aluminium chloride-35 or chlorine-35. Traces of chloroform-$^{35}Cl_3$ observed in the tetrachloromethane IR spectrum of the vapor were removed by further exposure of a solution of chlorine-35 in the chloro compound to UV light. A few milligrams of hexachloro-

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ethane-$^{35}Cl_6$ were recovered as by-product from the wall of the chlorination flask.

EXPERIMENTAL

Silver chloride-35. — The salt was prepared as described in reference 4 from sodium chloride-35 purchased from the U. S. Atomic Energy Commission, Oakridge, Tenn., U. S. A.

Aluminium Chloride-35Cl_3. — The salt was prepared from silver chloride-35 (2.645 g; 0.023 mol) as described in reference 4 in a tube with a cold finger condenser and sublimed thereon. The yield of sublimate in blank runs was about 90%.

Chlorine-35. — The element was prepared by oxidation of silver chloride-35 with dichromic acid as reported by Andersen [6].

Methyl Chloride. — Anhydrous aluminum chloride (1.33 g; 0.01 mole) in small lumps was added to 6.0 ml of methyl tosylate in a 25 ml round bottomed flask attached to a vacuum line via a stopcock and a trap cooled in dry ice and acetone to -78° and the system was evacuated to 0.1 mm. The mixture was heated gradually to 150° in a bath of Wood's Metal. Evolution of gas began even at 90° and was complete after one hr. The product was distilled from the U-tube into a graduated trap under vacuum. Yield : 1.3-1.4 ml. (Theor. 1.5 ml.) Fractional distillation on the vacuum line from a bath at -60° showed its vapor pressure was nearly constant. An IR spectrum of 15 mm of vapor in a cell 100 mm long showed only bands attributable to CH_3Cl.

Chloromethane-^{35}Cl. — The procedure for the preparation of the labelled compound had to be modified in such a way as to use the $Al^{35}Cl_3$ *in situ.* Although aluminium chloride is slightly soluble in CH_2Cl_2, $CHCl_3$, CCl_4 its chlorine has been reported to exchange rapidly with the solvents [4], thus precluding their employment in the present work. Aluminum chloride is very sparingly soluble in other solvents. Consequently the flask used to prepare the chloride was rapidly replaced by one containing 8.0 ml of methyl tosylate and the system was immediately evacuated. On slightly heating the tosylate it vaporized and condensed on the cold finger where it reacted with the aluminum chloride-35 to form methyl chloride-35 which was condensed in a U-tube on the vacuum line cooled to -78°. The crude product was freed of traces of hydrogen chloride by distillation through a tube filled with Ascarite. Yield : 0.75 ml. (82% of the theoretical amount.)

The residue was poured into concentrated ammonium hydroxide and chloride ion was precipitated with silver nitrate and recovered as silver chloride after acidification with dilute nitric acid. Only traces of AgCl were isolated.

Tetrachloromethane-35Cl_4. — A 1-l round bottomed flask with a slight depression on the bottom filled with water (20 ml) was attached to a vacuum

line via a stop-cock and evacuated. Two ml of chloromethane-^{35}Cl (0.04 mole) were distilled into the flask cooled in liquid nitrogen. The flask was then isolated by closing the stopcock and allowed to warm up to ambient temperature. In the meantime the rest of the vacuum line was filled with chlorine-35 to nearly one atmosphere. The pressure in the line was measured by a bellows manometer because chlorine rapidly attacks the surface of the mercury of an ordinary manometer. The chlorine in the line was then distilled into the flask which contained the chloromethane-35 until the pressure was 700 mm and the UV lamp was turned on. The pressure within the flask was observed by means of another bellows manometer. When it had fallen to a constant level more chlorine was admitted in the same manner. A total of 6.1 ml of chlorine-35 were brought into reaction. The tetrachloromethane-$^{35}Cl_4$, chlorine-35 and small amounts of incompletely chlorinated material were condensed in a trap on the line and the solution of chlorine-35 in the chlorinated hydrocarbons was irradiated for a few minutes with the UV lamp. A small amount of residual chlorine was removed by distilling the tetrachloromethane through a tube containing Ascarite. Traces of chloroform-$^{35}Cl_3$ were removed by freezing the tetrachloromethane and pumping off residual vapor. The yield of product was 2.4 ml (3.8 grams). Its IR spectrum showed no absorption in the CH stretching region. The reaction flask was washed out thoroughly with pentane and then with water. Separation and evaporation of the pentane layer left a residue of a few milligrams of hexachloroethane-$^{35}Cl_6$. The aqueous layer was treated with excess 10% aqueous silver nitrate solution to recover the chlorine-35.

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