Preparation of Deuterated tert-Butyl Chloride

The recent appearance of a note by Calf, Fisher and Garnett [1] on the exchange of cyclopentene and other olefinic hydrocarbons at 110° C in the presence of 6N deuteriochloric acid prompts us to report a convenient method of preparing deuterated tert-butyl chloride by exchange with 10N deuteriochloric acid. Apparently, the formation of the deuterated chloride proceeds by the same mechanism as that proposed by Garnett *et al.* [1] for cyclopentene since we have observed that when a 10N solution of deuteriochloric acid is stirred under an atmosphere of isobutene a good yield of deuterated tertiary chloride is obtained. Exchange of tert-butyl chloride is thus much more practical and economical than synthesis from hexadeuterioacetone and trideuteriomethylmagnesium iodide.

Attempts to deuterate tetraethyl carbinol, dimethylphenyl carbinol and methylphenyl carbinol by the same method were uniformly unsuccessful.

Experimental.

Deuteriochloric Acid.

Approximately 10N acid was prepared as described by Herber [2] from 4.2 moles of benzoyl chloride and an equivalent amount of deuterium oxide. The DCl evolved was absorbed in 350 ml of 99.8% deuterium oxide.

Deuterated tert-Butyl Chloride.

A mixture of 40 g (0.43 mole) of tert-butyl chloride and 350 ml of 10N DCl was stirred under reflux for 24 hours. Exchanged chloride was distilled off through a short Vigreux column and reheated under reflux with fresh 10N DCl. The rate of exchange was followed by measuring the IR spectrum of a sample. After three equilibrations there was virtually no absorption in the C-H stretching region. Recovery was nearly quantitative.

Deuterated tert-Butyl Chloride from Isobutene.

Deuteriochloric acid (100 ml of 10N) was stirred in a .5 l round bottomed flask under one atmosphere of isobutene for one day on a vacuum line. The chloride formed was distilled off into a trap after passage through a tube

filled with pellets of alkali. An IR spectrum of the chloride showed considerable deuteration had taken place.

Exchange in tert-butyl chloride therefore seems to occur by continuous elimination of HCl and addition of DCl to the isobutene present.

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