Liquid Phase Chlorination of 1,1,1-Trifluoropropane[1]

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We desired to obtain 3,3,3-trifluoro-1-chloropropane in quantity for the preparation of fluorinated silanes. (1) Vapor phase chlorination (2,3,4,5) of 1,1,1-trifluoropropane produces low yields of the mono- and dichloroderivatives, and is cumbersome on a large scale. We have developed a laboratory apparatus based on earlier works of E. Rapkin (6) for rapidly chlorinating 1,1,1-trifluoropropane in the liquid state to yield 65% of 3,3,3-trifluoro-1-chloropropane.

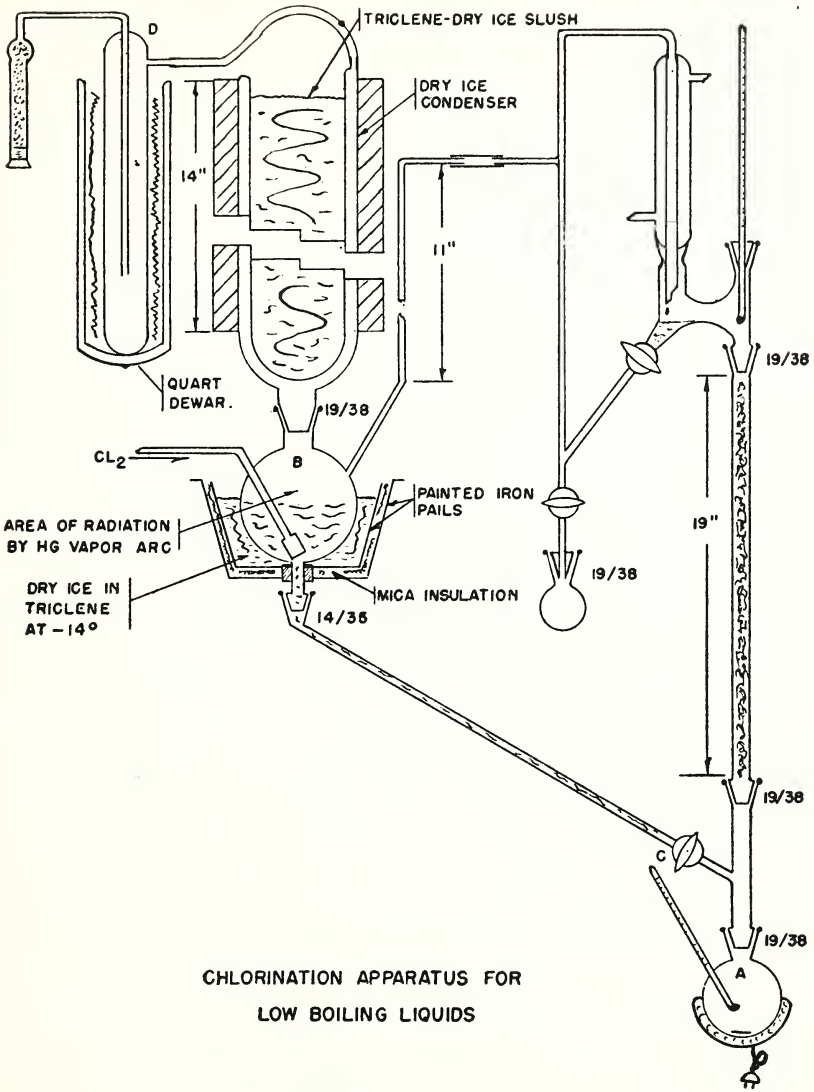
Experimental

The chlorination system (Fig. 1) was found to be completely free of pin holes by testing under vacuum with a Tesla Coil. Trifluoropropane, 444 g. (4.53 moles) was distilled from A to B, chlorine was passed in at a rate of 12.5 liters per hour, and the product was drawn off continuously at C. The solution was irradiated with a mercury arc 9″ from B and chlorine was admitted until a greenish yellow coloration appeared and finally disappeared when the temperature of B (thermometer well not shown) was raised to –14°. Chlorine was then passed in continuously at a rate of 12.5 l./hr. The temperature of the reaction mixture, B, was maintained as close to –14° as possible by addition of Dry Ice. At 15 min. intervals, approximately 25 ml. of the solution from B was drained into A, and at all times a small continuous stream was allowed to flow in this direction. Within 5 hrs. the temperature in B was allowed to rise to –8°. The entire contents of B were then drained into A, where the temperature was raised to 45°. This procedure was repeated at the 7, 8, 9, 12, 14, and 15 hr. points. Liquid condensate in trap D was distilled into B twice during the reaction. The reaction was discontinued at the 15½ hr. point, at which time liquid was refluxing into B from the Dry Ice-Triclene cooled condenser at a rate of 1 drop/3 sec. Five grams (1.12%) of trifluoropropane remained unreacted. There was obtained after rectification in an 18.5 plate glass-helices-packed column 21.5 g. (1.54%) of 1,1,1-trifluoro-2-chloropropane, b.p. 30°/750 mm., n_D^{20} 1.3158,(4)385 g. (65%) of 3,3,3-trifluoro-1-chloropropane, b.p. 46°, n_D^{20} 1.3300 (4) and 158 g. (21%) of 1,1-dichloro-3,3,3-trichloropropane (3,4). The significant infrared absorption maxima are listed in Table I.

INFRARED SPECTRA
MICRONS [a,b]

	C-F	C-M	C-F	C-F		C-C		C-H	C-Cl
$CF_3CH_2CH_3$	7.33m	7.75m	7.98s	8.65s	9.45w	9.75m	10.23w	13.40w	
CF_3—$CHClCH_3$	7.42m	7.87m	8.45s	8.80s	9.53m		10.18w	13.70w	15.40w
							12.25vw		
$CF_3CH_2CH_2Cl$	7.38m	7.80m	8.05s	8.65s	9.10m		10.30w	13.20w	14.87w
							10.75w		
$CF_3CH_2CHCl_2$	7.38m	7.80m	8.15s	8.70s	9.03m		10.90m	13.10m	14.60m
	7.70m				9.55m				

a. Absorption intensity: s, strong; m. medium; w, weak.
b. Determined with the Perkin-Elmer, model 21, Infrared Spectrometer.



CHLORINATION APPARATUS FOR LOW BOILING LIQUIDS

FIGURE 1

Summary

An improved liquid phase chlorination process has been developed for the preparation of 1-chloro-3,3,3-trifluoropropane.

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