



Fig. 3.—Heats of mixing in calories per mole of solution for the systems: chloroform with polyfluoro alkyl ethers.

The results obtained on mixing chloroform with the methyl, ethyl and *n*-propyl derivatives of 1,1,2-trifluoro-2-chloroethyl alkyl ethers are shown in Fig. 3 and Table I gives the heats of mixing per mole of solution at a mole fraction of 0.5.

TABLE I  
HEATS OF MIXING OF 1,1,2-TRIFLUORO-2-CHLOROETHYL ALKYL ETHERS WITH CHLOROFORM AT 0°

Ether	$\Delta H$ , cal./mole
Methyl	93 = 3
Ethyl	62 = 4
<i>n</i> -Propyl	52 = 3

The isopropyl derivative gave heat effects of the same magnitude as the normal compound. Sufficient material was not on hand for quantitative study. In contrast to the behavior shown by diethyl ether and acetone, the heats of mixing were small and positive. The slight cooling effect produced indicates the lack of formation of hydrogen bonds, at least in large numbers.

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### The Structure of Dioxadiene Dibromide

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Some time ago dioxadiene was found to react with only one molar equivalent of bromine to give a crystalline compound, dioxadiene dibromide, of unknown structure.<sup>2</sup> This was presumed to be 5,6-dibromo-*p*-dioxene. However, the possibilities that it had an oxonium bromide structure or that the dioxadiene ring had been ruptured were not excluded.

We have now found that I does not react with aqueous potassium iodide solution, a characteristic reaction of oxonium bromides.<sup>3</sup> Furthermore, I reacts with the magnesium-magnesium iodide dehalogenating reagent<sup>2</sup> and with phenylmagnesium bromide to regenerate dioxadiene in high yield. Thus the structure of I must be 5,6-dibromo-*p*-dioxene.

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(2) Summerbell and Umhoefer, *THIS JOURNAL*, **61**, 3020 (1939).

(3) McIntosh, *ibid.*, **32**, 1330 (1910).

**Attempted Reaction of I with Aqueous Potassium Iodide Solution.**—To a solution of 1.0 g. of potassium iodide in 20 ml. of water was added 0.5 g. of I. No iodine was liberated on heating at 60° for twenty-four hours.

**Reaction of I with Magnesium-Magnesium Iodide Reagent.**—In a two-necked flask fitted with a mercury-sealed stirrer and a side-arm connected to a condenser arranged for downward distillation were placed 10 g. of magnesium turnings and 75 ml. of anhydrous butyl ether. To this was added slowly 4 g. of iodine. The solution was heated until distillation started and to it was added dropwise a solution of 10 g. (0.04 mole) of I in 50 ml. of butyl ether. A total of 100 ml. of distillate was collected during this addition. Redistillation through a 10-cm. Vigreux column gave 3.4 g. (97%) of dioxadiene, b. p. 74–75°,  $n_D^{20}$  1.4351.

**The Reaction of I with Phenylmagnesium Bromide.**—To a solution of phenylmagnesium bromide prepared from 2.64 g. (0.11 atom) of magnesium and 17.3 g. (0.11 mole) of bromobenzene in 100 ml. of dry ether was slowly added a solution of 12.3 g. (0.05 mole) of I in 75 ml. of dry ether. After the moderately vigorous reaction subsided the mixture was allowed to stand for twelve hours and was then hydrolyzed by pouring into ice and ammonium chloride solution. The ether solution was separated and dried over magnesium sulfate. Distillation gave 5.9 g., b. p. 75–80°, and a sirupy residue. The distillate was dissolved in 50 ml. of carbon tetrachloride and to it was added dropwise a solution of bromine in carbon tetrachloride at 0° until a faint permanent color remained. Removal of the solvent *in vacuo* gave 9.6 g. of crystalline residue identified as I by mixture melting point. Assuming an average yield of 90% on the addition of bromine to dioxadiene this represents an 87% conversion to dioxadiene.

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### The Solubility of Aluminum Bromide in Cyclohexane<sup>1</sup>

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During the course of a study of the isomerization of cyclohexane with aluminum bromide catalyst, the solubility of aluminum bromide in cyclohexane has been determined.

**Materials.**—Aluminum bromide was prepared and distilled into glass ampoules in the manner described by Leighton and Heldman.<sup>2</sup>

The cyclohexane was the gift of the Shell Oil Company. The stated analysis as received was 99.7 vol. % cyclohexane (by correlation of freezing point and mass spectrograph analysis), 0.0003 wt. % sulfur, less than 0.0005 vol. % benzene and less than 0.001 vol. % phenols. The freezing point was 6.0°. This material was further purified by "freezing out" cyclohexane crystals, followed by percolation of the remelted crystals through silica gel. The "freezing out" was performed as follows: About 300 ml. of cyclohexane contained in a 500-ml. Erlenmeyer flask was placed in a cooling bath of ice and water, and, with frequent hand stirring and scraping, a thick slurry of cyclohexane crystals was produced. The crystals were filtered off, melted, and the process repeated. The resultant cyclohexane was percolated through a column of silica gel to remove water and any trace of olefins. The product was stored over sodium in brown glass bottles. Physical properties of the purified cyclohexane were: m. p. 6.5°,  $n_D^{25}$  1.4235.

(1) This work was supported by a grant from the Research Corporation.

(2) Leighton and Heldman, *THIS JOURNAL*, **65**, 2276 (1943).