

phenol in 82 ml. of 5% aqueous sodium hydroxide was added dropwise to 16.7 g. (0.11 mole) of phosphorus thiodichlorofluoride with shaking and water-cooling. The reaction mixture was stirred for an additional half hour and then allowed to stand at room temperature. The oil which separated was dissolved in 50 ml. of benzene and washed with 1.5% aqueous sodium hydroxide solution until neutral. The ben-

zene phase was dried over sodium sulphate, then the solvent was removed and the residual liquid fractionated in vacuo. Phenylphosphorochlorofluoridothioate, $n_D^{20} = 1.5298$, was obtained between 60–61°/5 mm. in 62% yield.

Anal. Calcd. Cl, 16.83; F, 9.02. Found: Cl, 16.45; F, 9.05.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

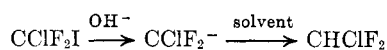
Methylene Derivatives as Intermediates in Polar Reactions. XX. The Reactions of Aqueous and Alcoholic Base with Chlorodifluoromethane and Difluoroiodomethane¹

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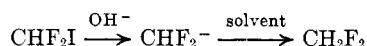
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We have reinvestigated a report that with 15% potassium hydroxide in ethanol for forty-eight hours at 35°, chlorodifluoromethane, chlorodifluoroiodomethane, and difluoroiodomethane gave no reaction, 24% chlorodifluoromethane, and 19% difluoromethane, respectively. It was found that chlorodifluoroiodomethane reacts essentially completely with ethanolic potassium hydroxide within a few minutes and that difluoroiodomethane yields no more than 5%, if any, difluoromethane. Rate constants were determined for the reaction of difluoroiodomethane with hydroxide ion in aqueous solution. From the results obtained it appears that the reaction is initiated by a concerted α -dehydroiodination to yield difluoromethylene directly in one step.

Haszeldine has reported that chlorodifluoromethane is stable to the action of 15% potassium hydroxide in 95% ethanol for forty-eight hours at 35°,² and that under the same conditions chlorodifluoroiodomethane yields 24% chlorodifluoromethane and that difluoroiodomethane yields 19% difluoromethane. Our observations that chlorodifluoromethane is quite reactive toward aqueous alkali,³ sodium methoxide⁴ and potassium isopropoxide⁵ caused us to doubt the first two reports. For the latter two reported reactions the mechanisms



and



were suggested.² In view of our evidence that attempts to generate the chlorodifluoromethyl anion instead bring about the concerted formation of the intermediate difluoromethylene and thence its reaction products,^{3,6} the reaction reported for chlorodifluoroiodomethane seemed improbable, and in view of our observation that α -fluorine is the least effective of the α -halogen substituents at

facilitating carbanion formation⁷ we doubted the formation of a methylene halide reported from difluoroiodomethane (but not chlorofluoroiodomethane nor fluorodiodomethane). We have therefore reinvestigated some of these points and also carried out some related experiments of interest.

RESULTS AND DISCUSSION

When solutions of chlorodifluoromethane and potassium hydroxide in ethanol are mixed at 35°, a copious precipitate of potassium chloride is formed within minutes. Titrations revealed that the theoretical amount of chloride ion ($\pm 5\%$) was formed within 5 minutes. This observation makes the report of a 24% yield of chlorodifluoromethane formed (from chlorodifluoroiodomethane) after 48 hours in ethanolic potassium hydroxide² difficult to understand.

The volatile products of the reaction of difluoroiodomethane with ethanolic potassium hydroxide were studied in a number of runs. Fluoriform, ethyl difluoromethyl ether, and varying amounts of starting materials were found, but no clear evidence for methylene fluoride formation could be obtained. Experiments with authentic methylene fluoride showed that not more than about 5% could have been formed and remained undetected.

In order to learn more about the mechanism of the reaction of difluoroiodomethane with base the kinetics of the reaction with aqueous sodium hydroxide were studied. This haloform proved to be

(1) This work was supported in part by the U. S. Atomic Energy Commission. For the preceding article in this series see J. Hine, A. D. Ketley, and K. Tanabe, *J. Am. Chem. Soc.*, in press.

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the most reactive that has been studied⁸ and for this reason and its relatively volatile character the rate constants obtained, particularly at the higher temperatures, are less reliable than most of those reported previously. The second-order rate constants observed are $(0.96 \pm 0.08) \times 10^{-2}$, $(6.0 \pm 0.4) \times 10^{-2}$, and $(51.8 \pm 4) \times 10^{-2}$ (all in l. mole⁻¹ sec.⁻¹) at 0°, 21.2° and 40°, respectively. Thus difluoroiodomethane is about one thousand times as reactive toward hydroxide ion in aqueous solution as is methyl iodide⁹ at the temperatures we have employed. As one α -fluoro substituent has been found to decrease the S_N2 reactivity of methyl halides,¹⁰ the reaction of difluoroiodomethane seems to be much too rapid to be proceeding by the S_N2 mechanism, and therefore more probably involves a dihalomethylene intermediate. Although the rate of carbanion formation that would be expected for difluoroiodomethane cannot be predicted very precisely, from the data obtained on related compounds^{7,8,11} it does not seem probable that the rate constant in water at 0° would be greater than about 10⁻³ l. mole⁻¹ sec.⁻¹ Thus, as difluoroiodomethane hydrolyzes faster than it would be expected to form carbanions, it hydrolyzes by a concerted mechanism in which there is no carbanion intermediate, but in which difluoromethylene is formed in a single step, as proposed earlier for bromodifluoromethane and chlorodifluoromethane.³

EXPERIMENTAL

Difluoroiodomethane. When mercuric fluoride was allowed to react with iodoform in the manner described previously in the preparation of fluorodiiodomethane,¹¹ about a 30% yield of difluoroiodomethane, b.p. 21–22°, was obtained from liquid collected in a Dry-Ice trap at the end of the system and from the forerun of the fluorodiiodomethane distillation. Ruff reported a boiling point of 21.6° for the compound.¹² Some material was also made by the reaction of mercuric fluoride with fluorodiiodomethane.

Reactions of chlorodifluoromethane. Chlorodifluoromethane¹³ was bubbled into 95% ethanol at room temperature to

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(13) The material used has been described previously.⁴

prepare a solution. When this solution at 35° was added to an equal volume of 15% ethanolic potassium hydroxide at the same temperature, a copious precipitate of potassium chloride began to form within a minute or two. After 10 min. the chloride formed from 10 ml. of the haloform solution was found to require 10.4 ml. of 0.0579*M* silver nitrate solution for titration. Another 10-ml. sample from the same solution was found to require 10.9 ml. of the silver nitrate solution after 1020 minutes.

Reaction of difluoroiodomethane. In a typical reaction with alcoholic potassium hydroxide, 1.0 ml. of difluoroiodomethane was added to 100 ml. of 15% potassium hydroxide in 95% ethanol in an apparatus designed to capture any gaseous products. A vigorous reaction immediately ensued and the infrared spectrum of the gaseous products, including those given off after the reaction solution was heated to boiling, revealed the presence of only fluoroform, ethyl difluoromethyl ether, and a little unchanged difluoroiodomethane. Because of similarities in absorption spectra, a little methylene fluoride could have escaped detection but not enough to account for more than a 5% yield. Separate experiments on methylene fluoride showed that under the reaction condition it would not have been decomposed and it would have been evolved as a gas from the reaction solution.

Kinetic runs. The kinetics of reaction of difluoroiodomethane with hydroxide ion in aqueous solution were studied by a method like that described previously for bromodifluoromethane.³ In a run at 0.0°, the first and sixth samples of haloform solution taken were found, by reaction with excess alkali, to be 0.04110 and 0.04080*N* in haloform. It was assumed that the haloform concentration in the other samples varied linearly in the order that the samples were taken. The data obtained in this run are listed in Table I. In most of the other runs made the rate constants fell to a greater or smaller extent than those given in Table I. We do not know the reason for this fall, but its existence suggests that the average rate constant may be less reliable than indicated by the average deviation. Because of the speed of the reaction and the volatility of the haloform, the rate constants obtained at higher temperatures may be even less reliable.

TABLE I
REACTION OF DIFLUOROIODOMETHANE WITH AQUEOUS SODIUM HYDROXIDE AT 0.0°

Time (sec.)	<i>N</i> ^a CHF ₂ I	[NaOH] _t ^b	100 k
507	0.04104	0.00785	1.130
801	0.04098	0.00712	1.032
1127	0.04092	0.00657	0.923
1500	0.04086	0.00578	0.924
2000	0.04074	0.00500	0.895
2880	0.04068	0.00405	0.830
			Average 0.956 ±
			0.084

^a The normality of haloform is 3 + *f* times the molarity.
^b [NaOH]₀ = 0.00987.

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