temperature was kept under 35° by external cooling. When the reaction became sluggish, more catalyst was added. Reduction was complete when a viscous yellow oil appeared and only a faint odor of nitrobenzene could be detected.[17] Water was added and the mixture placed in an ice–salt-bath. The yellow oil soon crystallized. The crude azoxybenzene was removed by rapid filtration. Some of the impurities oiled out leaving behind a yellow solid. The oil was chilled and the process repeated for an additional yield of crude azobenzene. The azoxybenzene was recrystallized from alcohol, yield 5.5 g. (65%), m.p. 34–35°. On a second recrystallization the product melted at 35–36°.

2,2'-Dimethylazoxybenzene.—To 10 g. of *o*-nitrotoluene (0.073 mole) was added 9 ml. of 100% hydrazine hydrate (0.18 mole) and 20 ml. of 95% ethanol. Some Raney nickel catalyst was introduced. There was much effervescence and the mixture turned slightly green, then yellow. The temperature of the reaction was kept under 35°. When the reaction became less vigorous, the solution was orange. More catalyst was added and the mixture allowed to stand at 0° overnight. The resulting orange-yellow crystals of 2,2'-dimethylazoxybenzene were collected by filtration and recrystallized from a mixture of alcohol and water. A second crop was obtained by adding water to the mother liquor, from the original filtration and treating the resulting dark orange-red oil with dil. HCl until it crystallized. The total yield was 3.2 g. (39%), m.p. 57.5–58.5°.[18]

4,4'-Dimethylazoxybenzene.—Ten grams of *p*-nitrotoluene (0.073 mole) was suspended in a solution of 9 ml. of 100% hydrazine hydrate (0.18 mole) and 30 ml. of 95% ethanol. Some Raney nickel catalyst was introduced and the mixture stirred for several hours. The *p*-nitrotoluene gradually dissolved and yellow crystals of 4,4'-dimethylazoxybenzene were deposited. When effervescence had ceased, the product was filtered and recrystallized from a mixture of alcohol and water. This yield was 3.4 g. (42%), m.p. 70–71°.[18]

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[17] If the reaction was allowed to proceed too far, an orange oil or a low melting solid was obtained which was impossible to purify by recrystallization.

[18] L. Zechmeister and P. Ron, *Ann.*, **468**, 117 (1929).

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

Methylene Derivatives as Intermediates in Polar Reactions. VIII. Difluoromethylene in the Reaction of Chlorodifluoromethane with Sodium Methoxide[1]

BY JACK HINE AND JOHN J. PORTER

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Since chlorodifluoromethane reacts with methanolic sodium methoxide 150 times as fast as chlorofluoromethane does at 35° despite the fact that α-fluorine substituents are known to decrease S_N2 reactivity, the reaction of chlorodifluoromethane is very probably not S_N2 in character. It is instead believed to involve an initial α-dehydrohalogenation to give difluoromethylene, a reactive intermediate that yields a mixture of methyl difluoromethyl ether and trimethyl orthoformate. The intermediate, methoxyfluoromethylene, appears to be involved in the production of the orthoformate. The α-elimination mechanism is further supported by the observation that while chlorodifluoromethane reacts only very slowly with sodium thiophenoxide alone, in the presence of sodium methoxide the reaction (which yields phenyl difluoromethyl sulfide) is relatively rapid. The thiophenoxide ion is found to be more than one hundred times as effective as methanol at combining with difluoromethylene.

Introduction

Chloroform and several other haloforms have been shown to undergo basic hydrolysis by the mechanism[2,3]

$$CHX_3 + OH^- \rightleftarrows CX_3^- + H_2O$$

$$CX_3^- \longrightarrow CX_2 + X^-$$

followed by rapid reactions of the intermediate dihalomethylene. This mechanism represents the principal reaction path only because such possible alternatives as the S_N2 mechanism[4] are considerably slower. Since α-fluoroalkyl halides are considerably more reactive by the S_N2 mechanism than are the analogous chloro, bromo and iodo derivatives,[5] it was of interest to learn whether the dihalomethylene (or α-elimination) mechanism is operative for such haloforms as chlorodifluoromethane.

Results and Discussion

The Reaction of Chlorodifluoromethane with Sodium Methoxide.—The only organic products observed in the reaction of chlorodifluoromethane and sodium methoxide in methanol were trimethyl orthoformate and methyl difluoromethyl ether. Although the difluoromethyl ether, a new compound, was not analyzed because of its tendency to decompose on standing, the following evidence exists for its structure. Its method of preparation is analogous to that used for ethyl difluoromethyl ether[6] and isopropyl difluoromethyl ether.[7] A survey in Lange's "Handbook of Chemistry" of twenty-seven series of methyl, ethyl and isopropyl compounds showed that the difference in boiling point between the methyl and ethyl compounds was 3.0 to 12.9° (av. 8.7 ± 2.6) greater than between the ethyl and isopropyl compounds. In view of this the boiling point of methyl difluoromethyl ether (−4°) is quite plausible considering the values reported for the ethyl (23.7°) and isopropyl (44.5°) analogs. Since an alkoxy substituent is known to activate a $-CF_2-$ group so that its acid hydrolysis

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[1] Ref. 7 is considered part VII. For part VI under a somewhat different series title see J. Hine, N. W. Burske, M. Hine and P. B. Langford, THIS JOURNAL, **79**, 1406 (1957). Much of the content of parts VIII and IX was presented in a talk at the Sixth Biannual Conference on Reaction Mechanisms, Swarthmore, Pennsylvania, September 13, 1956.

[2] J. Hine, *ibid.*, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[3] J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

[4] For the meaning of the term "S_N2" see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chap. 5.

[5] J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

[6] A. L. Henne and M. A. Smook, *ibid.*, **72**, 4378 (1950).

[7] J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957).

to a carbonyl group occurs readily,[6] we carried out the sulfuric acid-catalyzed hydrolysis of our material and identified methyl formate as a reaction product.

$$HCF_2OCH^3 \xrightarrow{H_2SO_4} HCO_2CH_3$$

Our structural assignment is also supported by the infrared spectrum of the compound and by stoichiometric considerations.

The methyl orthoformate and methyl difluoromethyl ether isolated accounted for 80% of the haloform that reacted (as measured by the amount of sodium chloride formed) in a synthetic experiment despite the fact that some of the volatile ether was undoubtedly lost. Assuming these are the only organic products, their relative yields may be calculated from the concentrations of methoxide ion used up and of chloride ion formed. Thus

$$f_o = \frac{\Delta[\mathrm{MeO}^-]}{2[\mathrm{Cl}^-]} - \frac{1}{2} \qquad (1)$$

where f_o is the fraction of the reacted haloform that gave methyl orthoformate. The analogous fraction in the reaction of potassium isopropoxide with chlorodifluoromethane was found to increase somewhat with increasing alkoxide ion concentration.[7] This apparently is true in the present case since a much higher fraction of methyl orthoformate was produced in the synthetic run, using concentrated sodium methoxide, than in the kinetic runs. Nevertheless, it was found that f_o does not change greatly during a kinetic run at the reactant concentrations we used. Assuming f_o constant, the following kinetic equation may be derived.

$$k = \frac{2.303}{t[a(1 + 2f_o) - b]} \log \frac{b(a - x)}{a[b - (1 + 2f_o)x]}$$

where $a = [\mathrm{CHClF_2}]_0$, $b = [\mathrm{MeO}^-]_0$, $x = \Delta[\mathrm{CHClF_2}]_t$, t = time and k is expressed in l. mole^{-1} (of haloform) sec.$^{-1}$. Typical kinetic data calculated from this equation are shown in Table I. The fall in rate constants with time probably is due to the loss of the volatile haloform (b.p. −40°) from the reaction solution, so that perhaps the value should be estimated as about 7.8 × 10^{-4}, by extrapolation to zero time.

TABLE I

THE REACTION OF CHLORODIFLUOROMETHANE WITH SODIUM METHOXIDE IN METHANOL AT 35°

$[\mathrm{CHClF_2}]_0 = 0.03721$; $[\mathrm{NaOMe}]_0 = 0.02918$; $f_o = 0.075$

Time, sec.	$[\mathrm{MeO}^-]$	10^4k, l. mole^{-1} sec.$^{-1}$
7595	0.02323	7.58
14478	.01913	7.84
29910	.01423	7.08
32270	.01362	7.06
60945	.00924	6.30
75802	.00707	6.69
	Av.	7.09 ± 0.41

In order to estimate how fast methoxide ion should react with chlorodifluoromethane by the S_N2 mechanism, we determined the approximate rate constant for the reaction of chlorofluoromethane with sodium methoxide. This rate constant was found to be about 4.5 × 10^{-6} l. mole^{-1} sec.$^{-1}$ and since α-fluorine is known to decrease S_N2 reactivity,[5] chlorodifluoromethane should react even more slowly if its mechanism were S_N2. Since it instead reacts more than 150 times as fast, the S_N2 mechanism seems implausible.

The reaction thus appears to be initiated by an α-elimination with the formation of a dihalomethylene.[8] The unreactivity of alkyl halides in general and of fluoroform in particular[3,7] shows that dehydro*fluorination* is probably only a minor side reaction. Hence the major reaction must be difluoromethylene formation. Some of the intermediate difluoromethylene adds methanol to yield methyl difluoromethyl ether and some reacts to give methyl orthoformate. The fact that f_o, the fraction of orthoformate, does not increase during a run shows that the difluoromethyl ether does not react further to give orthoformate. The orthoester is therefore very probably formed through the intermediate, methoxyfluoromethylene.[9] Thus we arrive at the reaction scheme

$$\mathrm{CHClF_2} + \mathrm{CH_3O^-} \longrightarrow \mathrm{CF_2} + \mathrm{CH_3OH} + \mathrm{Cl^-}$$

$$\begin{tikzcd}
\mathrm{CF_2} \arrow[r] \arrow[d] & \mathrm{CH_3OCHF_2} \\
\mathrm{CH_3OCF} \arrow[r] & (\mathrm{CH_3O})_3\mathrm{CH}
\end{tikzcd}$$

Capture of Difluoromethylene by Thiophenoxide Ions.—In order to bring a different sort of evidence to bear upon the reaction mechanism, we attempted to capture the intermediate difluoromethylene by use of the thiophenoxide ion, a reagent found previously to be effective at combining with dihalomethylenes.[2,3] We first studied the reaction of chlorodifluoromethane with sodium thiophenoxide alone. This was found to be a very slow process at 35° in methanol, the second-order rate constant being about 5 × 10^{-6} l. mole^{-1} sec.$^{-1}$. This small reactivity toward such a powerful nucleophilic reagent is itself added evidence that the 150-fold faster reaction with methoxide ion is not S_N2 in character, since in other S_N2 reactions the thiophenoxide ion has been found to be from twenty to ten thousand times as reactive as the methoxide ion.[5] Conclusive evidence against the S_N2 mechanism, however, was found in the observation that the reaction with thiophenoxide to give phenyl difluoromethyl sulfide was powerfully catalyzed by sodium methoxide. The presence of sodium methoxide caused the thiophenoxide to react as much as 60 times as fast as it would have in the absence of added base. Phenyl difluoromethyl sulfide was isolated in more than 60% yield in one run in the presence of added sodium methoxide.

We have made a quantitative estimate of the tendency of the thiophenoxide ion to combine with difluoromethylene as follows. Difluoromethylene might be expected to combine with any of the three nucleophilic reagents, methanol, methoxide ion or thiophenoxide ion. Neglecting that small though significant part of the reaction that proceeds far

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[8] For evidence that this α-elimination proceeds by a concerted mechanism, not involving a trihalomethyl carbanion, see J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957).

[9] The argument that this is so is analogous to that given briefly in ref. 7 and to be presented in more detail in a subsequent article.

enough to liberate fluoride ions, we may write

$$CF_2 + CH_3OH \xrightarrow{k_M} CH_3OCHF_2$$

$$CF_2 + CH_3O^- \xrightarrow[CH_3OH]{k_B} CH_3OCHF_2$$

$$CF_2 + C_6H_5S^- \xrightarrow[CH_3OH]{k_T} C_6H_5SCHF_2$$

From this reaction scheme (treating k_M as a first-order rate constant) and the assumption that difluoromethylene is formed only by the action of methoxide ion on the haloform, we may express the rate of reaction of thiophenoxide ion

$$\frac{d[C_6H_5S^-]}{dt} = k[CHClF_2][MeO^-] \left(\frac{k_T[C_6H_5S^-]}{k_T\,[C_6H_5S^-] + k_B\,[MeO^-] + k_M}\right) \quad (2)$$

and the rate of reaction of methoxide ion is expressed

$$\frac{d[MeO^-]}{dt} = k[CHClF_2][MeO^-] \left(\frac{k_B\,[MeO^-] + k_M}{k_T\,[C_6H_5S^-] + k_B\,[MeO^-] + k_M}\right) \quad (3)$$

Dividing eq. 2 by eq. 3

$$\frac{d[C_6H_5S^-]}{d[MeO^-]} = \frac{k_T\,[C_6H_5S^-]}{k_B\,[MeO^-] + k_M} \quad (4)$$

By the use of both acidimetric and iodimetric titrations the changes in thiophenoxide and methoxide ion concentrations may be determined. We now simplify eq. 4 by neglecting the reaction of difluoromethylene with methoxide ion, relating later how this neglect is justified. With this simplification eq. 4 becomes

$$\frac{dy}{dz} = (k_T/k_M)(T - y) \quad (5)$$

where $T = [C_6H_5S^-]_0$, $y = \Delta[C_6H_5S^-]$ and $z = \Delta[MeO^-]$. Integration of eq. 5 yields

$$(k_T/k_M) = \frac{2.303}{z} \log \frac{T}{T - y} \quad (6)$$

In Table II are shown data on a run, calculated according to eq. 6 which is based on the assumption that thiophenoxide ion is competing only with the solvent methanol for the intermediate difluoromethylene. If the methoxide ion had been a major competitor, the calculated values of k_T/k_M should increase as the reaction proceeds and the concentration of methoxide ion decreases. Since methanol is present at a concentration of about 25 *M*, the values of k_T/k_M found show that the thiophenoxide ion is more than 100 times as reactive.

TABLE II

REACTION OF CHLORODIFLUOROMETHANE WITH SODIUM THIOPHENOXIDE AND SODIUM METHOXIDE AT 35°[a]

Time, sec.	$[C_6H_5S^-]$	$[MeO^-]$	k_T/k_M
135	0.1509	0.2043	
2985	.1304	.1722	4.55
8235	.1153	.1452	4.55
21885	.1022	.1233	4.81
35790	.0997	.1040	4.13
70530	.0970	.1016	4.30
		Av.	4.47 ± 0.20

[a] $[CHClF_2]_0 = 0.1388$.

The numerous reports of difluoromethylene as an intermediate in gas phase reactions[10] certainly strengthen the evidence that it and other dihalomethylenes are intermediates in the hydrolysis of haloforms.

Experimental

Reagents.—Chlorodifluoromethane (Matheson Chemical Co.) and chlorofluoromethane (du Pont) were used directly from their cylinders without further purification. Infrared measurements showed that the chlorodifluoromethane contained less than 2% dichlorofluoromethane and less than 0.5% fluoroform. Methanol was purified by the method of Fieser, using magnesium.[11] The thiophenol (Matheson) used was found by iodimetric titration to be 99% pure. Turmeric yellow, rosolic acid and *p*-nitrophenol were all found to be satisfactory indicators for the titrations carried out in methanolic and aqueous methanolic solutions.

Products of Reaction of Chlorodifluoromethane with Sodium Methoxide.—Seventy-two grams (3.1 moles) of sodium was dissolved in about 600 ml. of methanol in a one-liter three-neck flask equipped with a fritted-glass gas-inlet tube and a −80° reflux condenser. Chlorodifluoromethane was then admitted to the flask rapidly causing an exothermic reaction. After 90 minutes the continual return of cold product from the reflux condenser had caused so much cooling that the reaction was proceeding rather slowly. Therefore the admission of haloform was interrupted and after allowing a few minutes for the residual haloform to react and the Dry Ice in the condenser to sublime the reaction flask was heated until methanol began to reflux, the more volatile products being collected in a trap at −80°. The admission of chlorodifluoromethane was resumed until the reaction appeared to be essentially complete and the distillation of volatile material repeated.

During the reaction a large amount of salt had precipitated from the reaction mixture. This was collected on a filter, washed with methanol, dried and found to weigh 130 g. Titration for chloride (Fajans) and fluoride[12] and for base showed that the material included 87.0 g. (1.49 moles) of sodium chloride and 42.4 g. (1.01 moles) of sodium fluoride and 0.01 mole of base. The methanolic filtrate was fractionally distilled through a 30-inch column packed with glass helices giving as the only products methanol containing some trimethyl orthoformate and pure trimethyl orthoformate (b.p. 98–99.5° at 740 mm.—infrared spectrum identical to authentic material). Including that material present in the methanol (analyzed by infrared measurements), 51 g. (0.48 mole) of trimethyl orthoformate was obtained.

The volatile material collected at −80° was distilled through a 2 ft. column packed with glass helices and equipped with condensers through which refrigerated glycol-water was circulated.

The fraction boiling at −4° at 740 mm. occupied 54 ml. at −80°, but it was clear that not all of the material was being condensed by the coolant which was at −8°. The material had infrared absorption maxima (in the order of decreasing intensity) at 9.53, 9.44, 8.97, 9.21, 8.18, 8.12, 8.25, 8.43, 8.84, 12.36, 12.21, 12.49, 7.29, 7.23, 7.58, 6.84, 7.64, 10.77, 6.89, 7.44, 3.43, 13.46 and 3.56 μ (gas phase). This difluoromethyl ether, like the other two reported, is rather unstable, decomposing on standing to liberate hydrogen fluoride. When about 0.5 ml. of sulfuric acid was added to about 10 ml. of the material refluxing at −4°, there was a slow evolution of gas that was not condensed in the −80° reflux condenser. Infrared measurements showed that this gas contained carbon monoxide. The reflux condenser was then removed, the difluoromethyl ether allowed to evaporate and the remaining solution heated to 50° with the evolution of gas. This gas, collected after passage through a short tube filled with sodium hydroxide pellets, had an in-

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(10) J. Dacey and J. Hodgins, *Can. J. Research*, **28B**, 90, 173 (1950); P. Venkateswarlu, *Phys. Rev.*, **77**, 676 (1950); R. K. Laird, E. B. Andrews and R. F. Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950); J. L. Margrave and K. Wieland, *J. Chem. Phys.*, **21**, 1552 (1953); and references cited therein.

(11) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, 1955, p. 289.

(12) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 721.

frared spectrum identical to that of methyl formate except for a band at 9.75 μ, probably due to silicon tetrafluoride.

From data on related compounds the density of methyl difluoromethyl ether at −80° is estimated as 1.10. Thus the yield of this product is 59 g. (0.72 mole) or 48% based on the haloform reacted (sodium chloride formed). Since a 32% yield of trimethyl orthoformate was obtained, 80% of the haloform that reacted was accounted for. From the relative yields of chloride and fluoride a 34% yield of the orthoester and 66% of the difluoromethyl ether would be expected.

Kinetics of the Reactions with Sodium Methoxide Alone.—Standard solutions of the organic halides were prepared by bubbling into methanol and weighing. The concentrations of several of the haloform solutions thus prepared were checked by titration for chloride ion in reactions that had proceeded well past 99% completion. For both compounds kinetic runs were carried out by adding a known volume of standard sodium methoxide to a large volumetric flask containing the halide solution and then withdrawing samples for analysis at known times.

From earlier experience on the reaction of bromofluoromethane with sodium methoxide[5] it was expected that the methyl fluoromethyl ether formed initially in the reaction of CH_2ClF might not react completely in the methanolic reaction solution but might hydrolyze if water were added during the analysis of samples. To minimize such hydrolysis, 10-ml. reaction samples were pipetted into 12 ml. of cold methanol and titrated quickly with less than 12 ml. of standard aqueous acid. When more water was added to a titrated sample, acid was liberated revealing the presence of the fluoromethyl ether. Rate constants were therefore calculated on the assumption that only one methoxide ion is used per halide molecule. The value ($4.5 \pm 0.6 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$) was obtained at 35°.

Since chlorodifluoromethane was considerably more reactive, its reaction samples were added to a known volume of standard acid to stop the reaction. The excess acid was then back-titrated. Appropriate experiments showed that the difluoromethyl ether does not solvolyze appreciably in largely aqueous solutions during the course of an hour, apparently because of a decrease in S_N1 reactivity brought about by the second fluorine atom.[13] The titrations could therefore be carried out with aqueous solutions. For eight points, when the acidimetric titration was complete, the concentration of chloride was determined by the Fajans method. The value of f_0 calculated from eq. 1 ranged from 0.0922 to 0.0672, decreasing slightly as the reaction proceeded. An intermediate value of 0.075 was used in calculating the rate constants. Although f_0 probably varies somewhat with the methoxide concentration, an initial concentration of about 0.03 M was used in all of our runs. The values of k obtained are not very sensitive to the exact value of f_0 used, particularly when the haloform is in excess as in our reactions.

Products of the Reaction of Chlorodifluoromethane with Sodium Thiophenoxide.—One hundred twenty-five grams (5.4 moles) of sodium was dissolved in about 800 ml. of methanol in a one-liter three-neck flask equipped with a stirrer, Dry Ice cooled reflux condenser and a gas dispersion tube. To the flask was added 112 g. (1.02 moles) of thiophenol with stirring and then chlorodifluoromethane was bubbled into the reaction mixture. At three times during the 7 hr. of reaction, the gas addition was discontinued, a sample from the reaction flask titrated acidimetrically and iodimetrically to follow the progress of the reaction, and the flask was warmed to remove the difluoromethyl ether that had formed. When all of the sodium methoxide had been destroyed, 0.10 mole of thiophenol remained unreacted. The completed reaction mixture was concentrated to about 300 ml. of a salt–liquid slurry by distillation and poured into about five liters of water. The heavy oily layer that separated was taken up in methylene chloride and washed with alkali. It was then combined with a second methylene chloride extract of the two aqueous layers and distilled until the methylene chloride was removed. Distillation of the residue yielded five fractions totaling 93.4 g. at pressures of 2 to 7 mm. and temperatures of 29 to 50° and 25.1 g. of a sixth fraction boiling largely at 165–185° at 1–2 mm. Fractionation of about 30 g. from samples four and five gave essentially entirely material, b.p. 62–63° at 7 mm., $n^{25}\text{D}$ 1.5084, d^{25}_4 1.2218, molecular refraction calcd. for $C_6H_5SCHF_2$ 38.69, found 39.11. Comparison of infrared spectra and refractive indices showed that practically all of the 93.4 g. was phenyl difluoromethyl sulfide (63% yield based on thiophenol that was used up).

The phenyl difluoromethyl sulfide structure is further supported by the infrared spectrum. Absorption maxima (in the order of decreasing intensity) were found at 9.32, 9.60, 13.55, 9.75, 14.50, 7.74, 9.14, 7.60, 13.06, 14.27, 9.99, 3.35 and 3.46 μ.

Distillation of the material at temperatures above about 60° gave a product that became cloudy and red upon standing. This appeared to be due to the presence of acid and could be prevented by storage over sodium carbonate or even by an alkaline wash. *Anal.* Calcd. for $C_7H_6SF_2$: C, 52.48; H, 3.78; S, 20.02; F, 23.72. Found: C, 52.20, 52.49; H, 3.83, 3.83; S, 20.22, 20.12; F, 24.59, 24.78.

Kinetics of the Reaction with Sodium Thiophenoxide.—Standard sodium thiophenoxide solutions were prepared by the addition of a weighed amount of thiophenol to a known volume of standard sodium methoxide, thiophenol being used in slight excess to produce the "sodium methoxide-free" sodium thiophenoxide. Runs were carried out like those with sodium methoxide alone except for the analysis of the reaction samples. This was done by titration to the *p*-nitrophenol end-point (both the sodium methoxide and thiophenoxide are neutralized in this titration) and then determining the thiophenol by titration with methanolic iodine using its own yellow color as the indicator.

The rate constant for the reaction of chlorodifluoromethane in the absence of sodium methoxide was calculated from the second-order rate equation assuming that one mole of thiophenoxide reacted per mole of haloform.

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[13] *Cf.* J. Hine and D. E. Lee, THIS JOURNAL, **74**, 3182 (1952).