TABLE I

PHYSICAL PROPERTIES OF PHENYLPYRIDINES

Diene		Isoprene	1,3-Pentadiene	2,3-Dimethylbutadiene	2-Me-1,3-pentadiene
Pyridinic product		2-Ph-4-methyl-	2-Ph-6-methyl-	2-Ph-4,5-dimethyl-	2-Ph-4,6-dimethyl-
$n^{25}D$		1.6103	1.6059	1.6062 (35°)	1.5993
B.p., °C. (mm.)		110-115 (3)	117-120 (4)	146-150 (6)	130-134 (4)
Picrate, m.p., °C.	Obsd.	185-187	129-130	202-203	186-188
	Lit.	162[a]	135[c]	.....	186-187[b]

[a] L. Musajo and M. Colonna, *Gazz. chim. ital.*, **62**, 894 (1932). [b] R. L. Frank and R. P. Seven, THIS JOURNAL, **71**, 2629 (1949). [c] R. L. Frank and P. W. Meikle, *ibid.*, **72**, 4184 (1950).

TABLE II

REACTION CONDITIONS, MATERIAL BALANCE AND YIELDS

Activated Alumina, Al-0501, Catalyst

Reactants, Benzonitrile + Diene	T, °C.	Catalyst, cc.	Contact time, sec.	Mole ratio $\left(\frac{RCN}{Diene}\right)$	Material balance Total input, g.	Material balance Recov., g.	Nitrile conversion (*A*), mole %	Pyridinic product Total, g.	Pyridinic product Yield, mole % calcd. on *A*	Pyridinic product Space-time yield[a] × 10⁴
1,3-Butadiene	400	78	3.9	1.2	85.8	85.0	12	2.81	27	117
Isoprene	405	78	4.5	1.0	65.4	65.1	12	5.64	63	179
1,3-Pentadiene	397	92	4.2	1.0	109.6	108.5	28	1.71	9.0	55
2-Methyl-1,3-pentadiene	398	97.5	3.2	1.0	109.2	107.1	28	7.82	26	218
2,3-Dimethyl-1,3-butadiene	395	78	4.1	1.0	132.5	128.4	12	5.64	53	193

[a] Defined as moles/hr./100 cc. catalyst.

the light of the catalyzed reaction mechanism discussed in an earlier paper.[3]

The yields of phenylpyridines calculated on the nitrile conversions (Table II) undoubtedly can be improved with further study. Thus, using a chromia–alumina catalyst, 2-phenylpyridine has been obtained in 60 mole % yield[4] as compared to 27 mole % in this work. This reaction offers a ready method for the synthesis of these phenylpyridines in small amounts. In addition to simplicity, the method is specific for the desired product, a direct contrast to the more recognized procedures in which mixtures of pyridines are formed.

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The Preparation and Properties of 2-Chloro-2'-fluorodiethyl Sulfide[1]

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As part of a program to discover new methods for the preparation of organic fluorine compounds, 2-chloro-2'-fluorodiethyl sulfide has been prepared and its properties investigated.

Attempts have been made by some British investigators to prepare the fluorine analogs of "mustard gas" by the action of thionyl fluoride and anhydrous hydrogen fluoride on thiodiglycol. The experiments were conducted in metal containers, with and without solvents, at high and low temperatures. No volatile fluorine compounds were obtained.

We have succeeded in preparing fair yields of the monofluoro compound by the series of reactions

$$HOCH_2CH_2SCH_2CH_2OH + 2COCl_2 \longrightarrow \underset{\text{I}}{ClCOOCH_2CH_2SCH_2CH_2OCOCl} + 2HCl$$

$$\text{I} + HF \longrightarrow \underset{\text{II}}{ClCOOCH_2CH_2SCH_2CH_2OCOF} + HCl$$

$$\text{II} + \xrightarrow{\text{heat}} \underset{\text{III}}{ClCH_2CH_2SCH_2CH_2F} + 2CO_2$$

The formation of thiodiglycol bis-chloroformate (I) proceeds smoothly at 0°. The replacement of chlorine by fluorine and the subsequent elimination of carbon dioxide have not been studied sufficiently to determine the optimum conditions. The main product of the over-all reaction (as now carried out) is the partially fluorinated derivative (III). Small amounts of what appears to be difluorodiethyl sulfide are obtained in admixture with the monofluorinated derivative; it appears as a low-boiling fraction in the distillation of the reaction product. The reason for the preferential formation of the monofluoroformate II, even when hydrogen fluoride is present in excess, is unknown.

2-Chloro-2'-fluorodiethyl sulfide, b.p. 91.5–92.5° (30 mm.), f.p. −44°, is a colorless liquid with a very faint, mercaptan-like odor which is not unpleasant. The molecular refraction calculated from the density and refractive index agrees with the value calculated from the atomic refractivities.

Experimental Part

Thiodiglycol Bis-chloroformate.—Liquid phosgene (110 g., 1.1 moles) was placed in a 500-ml. round-bottom flask fitted with a dropping funnel and surmounted by a reflux condenser cooled with an acetone–Dry Ice mixture. While the flask was cooled in ice-water, thiodiglycol (55 g., 0.5 mole) was added slowly through the dropping funnel. During this addition, which required about one hour, there was a copious evolution of hydrogen chloride. After the flask had stood at room temperature for four hours, it was connected to a water-pump; the pressure was reduced to remove any hydrogen chloride and excess phosgene. The colorless residual liquid thus obtained contains the correct amount of chlorine calculated for thiodiglycol bis-chloro-

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[1] This work was done in 1942 for the Office of Scientific Research and Development under Contract No. OEMsr-394 with the University of Chicago.

formate; all of the halogen is hydrolyzed by water. At room temperature, the bis-chloroformate decomposes at the rate of 5% per day, with the evolution of carbon dioxide to form mustard gas, 2,2′-dichlorodiethyl sulfide. At 50°, decomposition occurs at the rate of 50% in 24 hours. When the compound is stored in a steel bomb at 20°, the pressure developed corresponds to a decomposition rate of 4 to 5% per day.

The conversion of the bis-chloroformate to 2,2′-dichlorodiethyl sulfide was demonstrated as follows. A small amount of the completely decomposed material was distilled. All of it boiled between 104–106° under a pressure of 17 mm. The distillate melted at 14°; the recorded melting point of mustard gas is 15°. The identity of the product was further confirmed by converting it to a sulfoxide (m.p. 108–108.5° uncor.); the recorded m.p. of the known sulfoxide is 109.5° cor.

2-Chloro-2′-fluorodiethyl Sulfide.—Anhydrous hydrogen fluoride (90 g., 4.5 moles) was condensed in a copper flask surmounted by a copper reflux condenser equipped at the top with a dropping funnel and an outlet tube. Through the dropping funnel, 110 g. (0.5 mole) of thiodiglycol bis-chloroformate was added while the copper flask was maintained at −80°. After the addition was complete, the acetone-Dry Ice-bath was replaced by an ice-bath and the temperature allowed to rise to 0°. As the mixture warmed, there was a copious evolution of hydrogen chloride. After the mixture had stood for a day at room temperature, the temperature of the water-bath was raised slowly to 75°; during this period there was a vigorous evolution of carbon dioxide and hydrogen fluoride. The flask was then cooled, connected to a copper condenser arranged for distillation, and the reaction product distilled under reduced pressure, using an iron tube as a receiver. The temperature of the flask was raised slowly to 170°; during this slow distillation, there was a continued evolution of carbon dioxide and hydrogen fluoride. The 48 g. of colorless distillate was washed with water, dried over anhydrous sodium sulfate, and distilled under a pressure of 20 mm. The fraction boiling below 100° (25 g.) was refractionated at 30 mm. pressure. Two fractions were obtained. The first (b.p. 62.5 to 91.5°) is probably a mixture of difluorodiethyl sulfide and 2-fluoro-2′-chlorodiethyl sulfide.

Anal. Calcd. for $C_4H_8SF_2$: F, 30.1. Found: F, 18.0. Calcd. for C_4H_8SFCl: Cl, 24.9. Found: Cl, 13.0.

The higher boiling fraction distilled sharply between 91.5° and 92.5° (30 mm.). It weighed 16 g., a yield of 22%, d^{20}_{20} 1.228, n^{25}_D 1.4852.

Anal. Calcd. for C_4H_8SFCl: F, 13.3; Cl, 24.9; S, 22.4. Found: F, 13.9; Cl, 24.4; S. 22.0.

The molecular refractivity calculated from the density and refractive index is 33.1; the value calculated from the sum of the atomic refractivities is 33.4.

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Acid-catalyzed Hydrolysis of Acetal and Chloroacetal[1]

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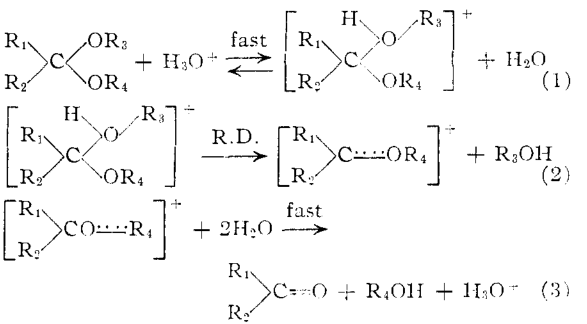
In the course of a study of the relative rates of acetal and ketal hydrolysis,[2] the acid dependence and solvent isotope dependence of the rate has been investigated. The results provide additional support for the mechanism of O'Gorman and Lucas.[3,4] This present work also extends the range of this mechanism, shown in equations 1–3, to a 50% dioxane–water mixture.



Previously reported evidence supporting this mechanism is: (1) there is no racemization at the alcohol carbon[3,5,6]; (2) the reaction exhibits specific hydronium ion catalysis in water[7]; (3) the second-order rate constant is larger by a factor of three in deuterated water[8]; (4) the rate is a linear function of H_0 with unit slope, indicating that no water molecules are firmly bound in the transition state.[9-13]

The present work shows that the rate of hydrolysis of chloroacetal, like that of methylal[9] and ethylal,[11] has the indicated acid dependence, that the hydrolysis of acetal in 50% aqueous dioxane is likewise faster by a factor of three when deuterated water is used, and that acetal hydrolysis in 50% aqueous dioxane is catalyzed only very slightly if at all by molecular formic acid.

Results

***H_0* Dependence.**—The acid dependence of the rate of hydrolysis of chloroacetal (in a solvent containing 4% dioxane) is shown in Table I. The last column of this table is expected by theory[12,13] to be approximately constant. As with methylal[9] and ethylal[11] the rates in the more concentrated hydrochloric acid solutions are somewhat higher than predicted by theory. With methylal this deviation was shown to be caused by a specific effect of chloride ion on the activity of the substrate,[9b] and the same is very likely true in the present case. Four concentrations of perchloric acid, sulfuric acid, and the most dilute hydrochloric acid give constant values of ($\log k_1 + H_0$) of acceptable precision.

Solvent Isotope Effect and General Acid Catalysis.—The second-order rate constant for the hydronium ion catalyzed hydrolysis of acetal in 50% dioxane–water[14] is 0.248 ± 0.004 l. mole^{-1} sec.$^{-1}$ at 25.0°. Replacing the water by an equal volume of D_2O increases this rate to 0.765 ± 0.050 l. mole^{-1} sec.$^{-1}$, indicating that a prototropic equilibrium

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[1] The work herein reported was carried out on Project NR055-328 between the Office of Naval Research and the Pennsylvania State University.

[2] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, forthcoming.

[3] J. M. O'Gorman and H. J. Lucas, *ibid.*, **72**, 5489 (1950).

[4] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 334.

[5] H. K. Garner and H. J. Lucas, THIS JOURNAL, **72**, 5497 (1950).

[6] E. R. Alexander, H. M. Busch and G. F. Webster, *ibid.*, **74**, 3173 (1952).

[7] J. N. Brönsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[8] W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 330 (1937).

[9] (a) D. McIntyre and F. A. Long, THIS JOURNAL, **76**, 3240 (1954); (b) F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954).

[10] Although W. W. Kaeding and L. Andrews, *ibid.*, **74**, 6189 (1952), interpreted their work in terms of another mechanism it is nicely consistent with eq. 1–3 if it is assumed that the intermediate oxo-carbonium ion reacts with ethanol about as readily as with water.

[11] P. M. Leininger and M. Kilpatrick, *ibid.*, **61**, 2510 (1939).

[12] L. P. Hammett and M. A. Paul, *ibid.*, **56**, 830 (1934).

[13] L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

[14] The exact composition of this solvent mixture is described in the Experimental part.