of the layers, addition of potassium carbonate to the acid solution and extraction with chloroform, the washed and dried chloroform solution was distilled *in vacuo*. After a fore-run of unreacted 2-aminopyridine, the fraction boiling at 185–205° and 0.5 mm. was collected and crystallized from ligroin; yield 3.4 g. (42% based on recovered 2-aminopyridine), m.p. 131–133°. Recrystallization raised the m.p. to 133–135°, undepressed upon admixture with a specimen prepared by procedure a; identity was confirmed by infrared comparison.

Ultraviolet Absorption Spectra.—All spectra were determined in 95% ethanol solution: 1-phenacyl-2-pyridinethione (VIa)—$\lambda_{max.}$ 243, 285 and 365 mμ (log ϵ 4.20, 4.12 and 3.78); $\lambda_{min.}$ 265 and 315 mμ (log ϵ 3.75 and 3.43).

2-Pyridinethiol: $\lambda_{max.}$ 285 and 363 mμ (log ϵ 3.94 and 3.64); $\lambda_{min.}$ 245 and 315 mμ (log ϵ 2.89 and 3.07).

1-Ethyl-2-pyridinethione: $\lambda_{max.}$ 287 and 360 mμ (log ϵ 4.12 and 3.86); $\lambda_{min.}$ 245 and 315 mμ (log ϵ 2.70 and 3.37).

2-(2-Pyridylthio)-acetophenone (Va): $\lambda_{max.}$ 247 and 288 mμ (log ϵ 4.36 and 3.76); $\lambda_{min.}$ 270 mμ (log ϵ 3.59).

1-(2-Pyridylthio)-4-dialkylamino-2-butanones (Vb–d): λ_{max} 245 and 290 mμ (log ϵ 4.03 and 3.67); $\lambda_{min.}$ 265 mμ (log ϵ 3.28).

2-Ethylthiopyridine: $\lambda_{max.}$ 250 and 293 mμ (log ϵ 3.90 and 3.54); $\lambda_{min.}$ 270 mμ (log ϵ 3.16).

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Lauraldehyde. Hemiacetal Formation

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Lauraldehyde has been reported to exist in two crystalline forms, m.p. 11° and 44.5°. It is shown in this report that the higher melting form is identical with the hemiacetal of lauraldehyde and lauryl alcohol.

Krafft[1] decomposed thermally a mixture of the barium salts of lauric and formic acids and obtained a substance which he described as lauraldehyde, m.p. 44.5°. Many years later Zaar[2] employed the same reaction and found that the product contained lauryl alcohol which was shown to form with lauraldehyde a crystalline substance which melted at 44.5–45.5° and had the composition of the hemiacetal. It was stated, however, that this product was not identical with the one obtained by Krafft. The lauraldehyde prepared by Zaar was a liquid, m.p. 11°, which deposited a quantity of crystals, m.p. 44.5°, on standing, and this substance was considered to be identical with Krafft's lauraldehyde. It was converted in part into the liquid aldehyde by vacuum distillation. The molecular weights of both solid and liquid aldehydes were found to be in good agreement with the theoretical value for lauraldehyde. Both gave the same oxime and semicarbazone, and from such convincing evidence Zaar concluded that lauraldehyde existed in two monomeric forms, differing only in physical properties.

Our experiments show that lauraldehyde and lauryl alcohol readily combine to form the hemiacetal which corresponds in analysis, molecular weight, physical properties and chemical behavior to the substance, m.p. 44.5°, reported by Zaar. This hemiacetal yields lauraldehyde semicarbazone and a phenylurethan which is identical with that obtained from lauryl alcohol.

It seems very probable from these results and from the failure of a number of methods to convert lauraldehyde, m.p. 11°, into a higher melting form, that the higher melting form reported by earlier workers was in fact the hemiacetal of lauraldehyde and lauryl alcohol.

The hemiacetal is soluble in acetone and ether in which it is apparently highly dissociated, while it has a limited solubility in lauraldehyde where, owing to the high concentration of aldehyde, the equilibrium favors the hemiacetal. The molecular weight of the hemiacetal, determined cryoscopically in benzene, indicates nearly complete dissociation. Upon distillation of the hemiacetal, the forerun is very rich in lauraldehyde and as distillation continues the distillate becomes richer in lauryl alcohol. Experiments were conducted to determine the conditions for precipitation of the hemiacetal, and it was found that no more than 5.0 g. of lauryl alcohol may be added to 100 g. of lauraldehyde (aldehyde content 99.8%) without precipitation of the hemiacetal at temperatures below 19°, and that no more than 7.2 g. of the alcohol may be added at temperatures below 24°.

The infrared spectrum of the hemiacetal in carbon tetrachloride has the following discernible features: –OH absorption at 3350 and 1060 cm.$^{-1}$, C=O absorption at 1735 and 2740 cm.$^{-1}$, C–O–C absorption at 1120 cm.$^{-1}$, and suggests an equilibrium between the hemiacetal and its dissociation products, lauraldehyde and lauryl alcohol.

Experimental Part

Hemiacetal Formation.—Lauraldehyde (Givaudan-Delawanna, Inc.), b.p. 104–109° (6 mm.), aldehyde content (hydroxylamine method) 95.98%, acid value 4.01, was shaken with a saturated solution of sodium bisulfite for one hour. The resulting addition product was collected, washed with cold water, ethyl alcohol and ether. The bisulfite compound was decomposed with sodium carbonate, and the aldehyde was extracted with ether. Concentration of the dried extracts gave an oil which was fractionated to yield a main fraction, b.p. 99.5–100.0° (3.5 mm.), $n^{24.7}{}_{D}$ 1.4328, aldehyde content 99.8%, acid value 0.57. A mixture of 10 g. of this aldehyde and 10 g. of lauryl alcohol was heated at 50° for a period of 30 minutes. Upon cooling, immediate precipitation of a white, waxy solid occurred. After recrystallization from acetone the product melted at 43.7–44.0°; yield 15.9 g. (80%). Bases strongly catalyze the formation of the hemiacetal at room temperature.

Anal. Calcd. for $C_{24}H_{50}O_2$: C, 77.77; H. 13.60; mol. wt., 370.6. Found: C, 77.68; H, 13.72; mol. wt. (benzene), 204.4, 196.7, 195.1.

The hemiacetal gave lauraldehyde semicarbazone, m.p. 102–104°, and a phenylurethan, m.p. 76°, which was identical with the phenylurethan prepared from lauryl alcohol.

Thermal Decomposition of the Hemiacetal.—A small quantity of the hemiacetal (16.5 g.) was fractionated under reduced pressure. The fractions obtained were analyzed for lauraldehyde content by the hydroxylamine method.

Fraction, b.p., °C. (mm.)	Grams	Lauraldehyde, %	Wt., g.
102.4–107.2 (4.5)	5.7	73.4	4.18
107.2–113.1	3.9	55.1	2.15
113.1–116.0	3.9	31.9	1.24
Residue (above 116°)	3.0	17.1	0.51
Total	16.5		8.08

Solubility of the Hemiacetal in Lauraldehyde.—To 5.0 g. of lauraldehyde (aldehyde content 99.8%) was added 0.25 g. of lauryl alcohol. The reaction mixture was warmed at 40° for a few minutes and upon cooling to 15° gave a heavy precipitate of the hemiacetal, which dissolved upon warming to 20°. Upon cooling to 19.0° and inoculating the solu-

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[1] F. Krafft, *Ber.*, **13**, 1413 (1880); **23**, 2360 (1890).

[2] B. Zaar, *J. prakt. Chem.*, **132**, 163 (1931).

tion with crystals, a faint precipitate barely was discernible even after several hours. The precipitate was much more evident upon cooling to 18.5° and disappeared entirely upon warming to 19.5°. On this basis it is evident that no more than 5.0 g. of lauryl alcohol may be added to 100 g. of lauraldehyde (4.76% solution of the alcohol) without causing precipitation of the hemiacetal at temperatures below 19.0°. The experiment was repeated using 0.36 g. of lauryl alcohol in 5.0 g. of lauraldehyde, and it was found that precipitation of the hemiacetal occurs if more than 7.2 g. of lauryl alcohol is added to 100 g. of lauraldehyde (6.71% solution of the alcohol) at temperatures below 24°.

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Polarographic Behavior of 2,2,2-Trichloroethanol. Acidic Nature of Trichloroethanol

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As part of a systematic investigation of the effect of various functional groups upon the electrochemical fission of carbon–halogen bonds, the polarographic behavior of the chloroethanols was investigated in order to extend the available data. Only 2,2,2-trichloroethanol of the three 2-chloroethanols gave a polarographic wave in the potential range of 0 to −2.0 v.

One cathodic wave was obtained for trichloroethanol in buffered solution over the *p*H range of 6.0 to 12.4 (Fig. 1); no wave was observed at lower *p*H due to prior hydrogen discharge. No chloroethanol (ethylene chlorohydrin) reduction was observed over the same range. The absence of a second wave of trichloroethanol indicates that dichloroethanol also is not reducible under the conditions studied.

Values of α (calculated from the relation $E_{1/4} - E_{3/4} = 0.056/\alpha$ at 25° and $0.051/\alpha$ at 0°) varied from 0.2 to 0.3 at 60-cm. head and 0.3 to 0.4 at 90-cm. head; values of n evaluated on the basis of the Ilkovic equation were 2.0 ± 0.2.

The $I(i_d/Cm^{2/3}t^{1/6})$ *vs.* *p*H relation (Fig. 1) shows that the current varies considerably in different buffers even at the same *p*H. However, I is essentially constant in a given buffer up to *p*H 11; the decrease at higher *p*H may be due to the smaller diffusion coefficient resulting from anion formation. Hydrolysis is not involved since no measurable decrease in current was observed in any solution upon standing for an hour. The largest I values are found in NH_3 buffers and KCl–NaOH solutions, slightly smaller values in borate, and the smallest in phosphate-containing buffers. The latter decrease may be due to formation of a phosphate compound, as has been noted with chloroethanol.[1]

Polarographic Determination of Trichloroethanol.—The linear relationship between current and concentration (0.1 to 1.0 m*M*) in ammonia buffer at *p*H 8.4 indicates that trichloroethanol can be determined polarographically; under ideal conditions, analytical results accurate to ±2% can be obtained.

Nature of the Reduction Process.—The variations of current with temperature and with drop-time (height of mercury) indicate the current-producing process to be diffusion controlled.

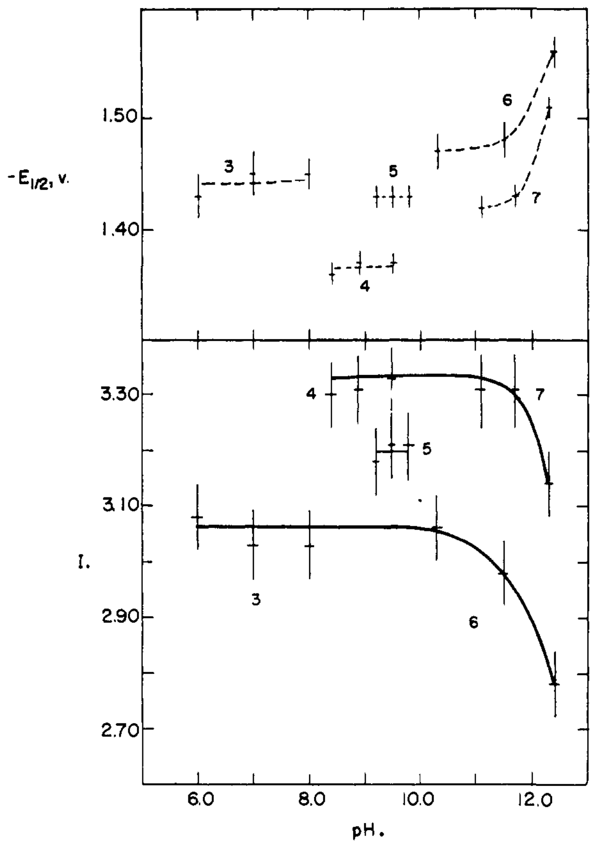

Fig. 1.—Variation of $E_{1/2}$ and I (diffusion current constant) with *p*H for trichloroethanol at 25° and 60 cm. Concentration of the alcohol was 0.5 m*M*. The numbers refer to the buffers listed in Table I. The size of each point indicates the possible uncertainty.

Application of the Ilkovic equation (diffusion coefficient calculated by Stokes–Einstein equation) and coulometric runs (ammonia buffer at *p*H 8.4) indicate the reduction process to involve two electrons per molecule. The two-electron wave of trichloroethanol could conceivably be due to carbon–chlorine or carbon–hydroxyl bond fission with the formation of 2,2-dichloroethanol or 1,1,1-trichloroethane. The fission of the carbon–hydroxyl bond is rather unlikely in this case since the weaker bond (the bond becomes weaker as the acidity decreases) of chloroethanol and ethanol is non-reducible under similar conditions. Polyhalogenated organic compounds generally show a stepwise reduction of carbon–halogen bonds,[2] *e.g.*, with a compound such as ethyl trichloroacetate the first chlorine comes off more readily than the second one, which in turn comes off more readily than the third. Of the three waves, the more negative ones correspond to the two waves of ethyl dichloroacetate, and the most negative wave corresponds to the one wave of ethyl chloroacetate. Therefore, the following over-all electrode reaction probably accounts for the observed behavior

$$Cl_3C{-}CH_2OH + 2e^- + H^+ \longrightarrow Cl_2CH{-}CH_2OH + Cl^- \quad (1)$$

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[1] R. H. A. Plimmer and W. J. N. Burch, *J. Chem. Soc.*, 286 (1929).

[2] P. J. Elving, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), **14**, 99 (1953).