100 ml with methanol–chloroform (9:1, v/v) and its absorbance was determined at 262 nm. After the yellow solution was exposed to laboratory fluorescent light for 2 hr, it was stored in the dark at room temperature for 65 hr. Its absorbance at 330 nm was then measured, from which the concentration of *trans* ester (and hence of the original *cis* ester) was calculated using 32,000 as the extinction coefficient.

Registry No.—**3c**, 22286-74-4.

Oxygen-Transfer Reactions of Amine N-Oxides. IV. The Pyridine N-Oxide–Trichloroacetic Anhydride Reaction

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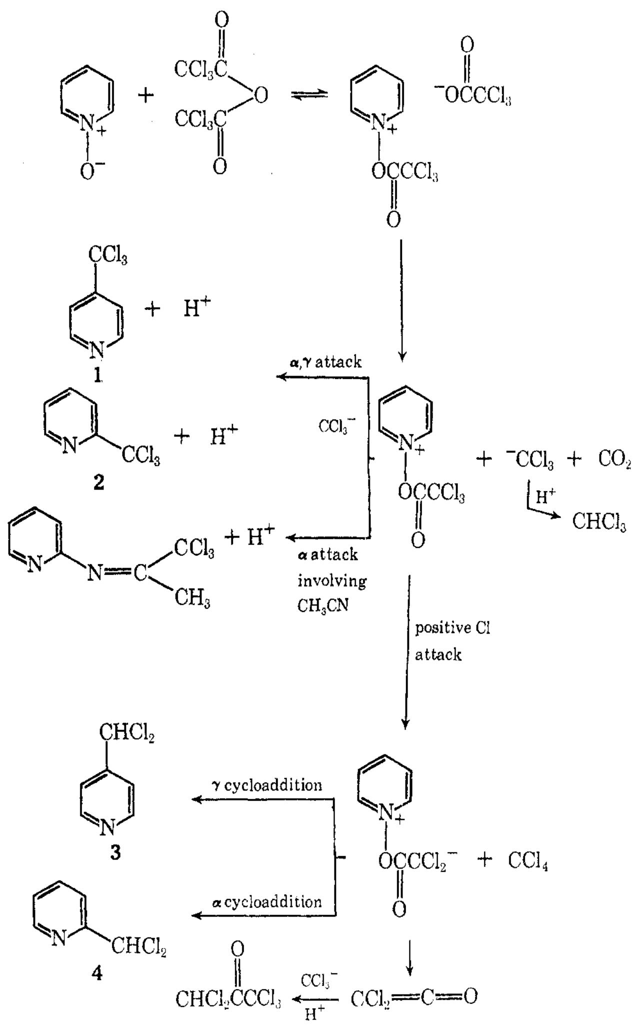
During the course of our general studies[2] on the reactions of N-oxides with acylating agents, we observed[3] a rather unusual reaction between trichloroacetyl chloride and picoline N-oxides which gives picolyl chlorides and carbon dioxide in fairly high yields after a few hours in refluxing chloroform. The chloride product was found to be a result of the high susceptibility of trichloroacetate esters to displacement by chloride ion, and the carbon dioxide was found to be a result of the unexpectedly fast rate of decarboxylation of ammonium trichloroacetate salts in solutions at high concentration. The present report deals with an additional manifestation of the rapid decarboxylation rate of the trichloroacetate ion in the reaction of pyridine N-oxide with trichloroacetic anhydride.

When pyridine N-oxide is refluxed in chloroform in the presence of trichloroacetic anhydride, no appreciable reaction is evident even after several hours. The N-oxide can be largely recovered after such a period. However, when the two reagents are mixed in acetonitrile solvent even at 0°, an exothermic reaction is immediately evident and carbon dioxide evolution begins at once. If the temperature is maintained at 0°, the gas evolution levels off at *ca.* 30%. When the reaction is carried out at 20–30°, 1 equiv of gas is evolved after *ca.* 5 hr.

The resulting product solution contains an exceedingly complex mixture of substituted pyridine derivatives. The products isolated and identified after the complicated work-up procedure, summarized in the Experimental Section, are carbon tetrachloride (40%), chloroform (20%), pentachloroacetone (20%), α-trichloromethylpyridine (10–20%), γ-trichloromethylpyridine (1–4%), α-dichloromethylpyridine (present), γ-dichloromethylpyridine (5%), and α-aminopyridine (4%). These yields are based on amount of N-oxide present initially, since 2 equiv of the anhydride were used in the runs in which quantitative analyses were attempted. No detectable amount of α-trichloroacetoxypyridine, which was synthesized independently, was observed by nmr or infrared. This product is the expected one based on analogy with the acetic anhydride–pyridine N-oxide reaction.[4]

The reaction at hand is apparently not a result of homolytic cleavage of the N–O bond of the acylated N-oxide, since very little carbon dioxide is obtained when the N-oxide is treated with trichloroacetyl chloride. A more likely explanation is that the driving force for the reaction is the exothermic loss of carbon dioxide from free trichloroacetate ion, which is not complexed with its counterion. Scheme I uses this idea in *rationalizing* the products observed.

Scheme I



That the observation of any reaction at all is definitely coupled to the polarity of the medium was evidenced by slow addition of acetonitrile to a refluxing solution of the reagents in chloroform. Only when the solvent mixture contains *ca.* 50% acetonitrile does carbon dioxide evolution occur at an appreciable rate. The spectral properties of the product residues from

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these conditions were similar to those from the acetonitrile runs but were not investigated further. This serves to militate against acetonitrile functioning in any stoichiometric way. A more likely role is a polarity effect which allows formation of free trichloroacetate ion. The proposed scheme is by no means uniquely established by experimental facts. Alternative radical chains and carbene mechanisms are also possible. It does seem clear that trichloroacetate ions can be more reactive toward decarboxylation than toward what would seem to be a facile nucleophilic atack on a charged pyridine derivative.

The formation of α-aminopyridine could be a result of attack of one of the pyridine bases on the N-acetoxy pyridinium species, but the product in such cases would not be expected to hydrolyze as readily as the Schiff-base structure shown. The failure of the acid chloride reaction militates against a heterolytic cleavage of the acetoxonium ion with α attack by solvent, as has been observed[5] in picoline N-oxide reactions using benzonitrile solvents. The decarboxylation of pyridinium trichloroacetate[8] does not give **1**, and the anhydride does not react with pyridine to the products found here under similar conditions.

Experimental Section

Infrared spectra were obtained using a Beckman IR-5 spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer. Glpc analyses of chloroform and carbon tetrachloride were carried out at 50° using an Aerograph 90-P and a 10 ft × 0.125 in. column packed with 20% TCEP on firebrick. Analyses were obtained from Berkeley Analytical Laboratories, Berkeley, Calif. Pyridine N-oxide was distilled directly into the reaction flask. Trichloroacetic anhydride was distilled, bp 60° (0.6 mm), immediately before use. Acetonitrile was dried by distillation from phosphorus pentoxide.

2-Trichloromethylpyridine (2).—This compound was synthesized by the reaction of 2-picoline with chlorine in acetic acid–sodium acetate[6] and obtained as an oil, bp 98° (15 mm). Nmr spectra of carbon tetrachloride solutions showed the characteristic pattern of a 2-substituted pyridine, an H-6 doublet of doublets at δ 8.71 ($J = 4.2$ Hz, $J' \cong 1.5$ Hz) and H-3, -4, and -5 multiplets centered at δ 7.87 and 7.33. It failed to form a picrate.

Anal. Calcd for $C_6H_4NCl_3$: C, 36.67; H, 2.05; N, 7.12; Cl, 54.14. Found: C, 36.92; H, 2.05; N, 6.98; Cl, 53.98.

4-Trichloromethylpyridine (1).—The sequence[7] identical with that used for **2** afforded **1** as an oil, bp 78° (10 mm). Nmr spectra of carbon tetrachloride solutions of this material showed the characteristic four-substituted pattern (AA'XX' system), δ_A, α protons, 8.87, and δ_X, β protons, 8.00 ($J = 4.5$ Hz, $J' \cong 1.8$ Hz). It formed a picrate, mp 151–152° (lit.[7] mp 154°).

2-Dichloromethylpyridine (4).—Authentic **4** was obtained by reduction[7] of **2**, using stannous chloride, as an oil, bp 90–92° (18 mm). Its nmr spectrum in carbon tetrachloride showed the ω-proton singlet at δ 7.01, an H-6 multiplet at δ 8.65, and H-3, -4, and -5 multiplets at δ 7.87 and 7.39. It formed a picrate, mp 115.5–116° (lit.[8] mp 115–116°).

4-Dichloromethylpyridine (3).—Authentic **3** was obtained[7] in low yield from the stannous chloride reduction of **1** as an oil, bp 78–80° (15 mm). Its nmr spectrum in carbon tetrachloride showed the ω-proton singlet at δ 6.81 and the characteristic AA'XX' pattern of a 4-substituted pyridine, δ_A, α protons, 8.63, and δ_X, β protons, 7.40 ($J = 4.0$ Hz, $J' \cong 1.5$ Hz). It formed a picrate, mp 135–136°.

Anal. Calcd for $C_{12}H_8Cl_2N_4O_7$: C, 36.84; H, 2.06; Cl, 18.13; N, 14.32. Found: C, 36.65; H, 1.97; Cl, 18.28; N, 14.14.

α-Trichloroacetoxypyridine.—This material was prepared by treatment of an ether suspension of the silver salt of 2-pyridone with trichloroacetyl chloride. The product was distilled, bp 58° (0.7 mm). Its infrared spectrum in chloroform showed carbonyl absorption at 1767 cm^{-1}. The nmr spectra of carbon tetrachloride solutions of this material showed the characteristic pattern of a 2-substituted pyridine, an H-6 doublet of doublets at δ 8.41 ($J = 4$ Hz, $J' \cong 2$ Hz) and H-3, -4, and -5 multiplets centered at δ 7.50 and 7.25. The chemical shift of H-6 is distinctly different from that of the products (**2** and **4**) obtained here.

Pyridine N-Oxide–Trichloroacetic Anhydride Reaction.—The anhydride (36.00 g, 0.117 mol) in 20 ml of acetonitrile was added over a 10-min period to 160 ml of solvent containing 5.57 g (0.059 mol) of freshly distilled pyridine N-oxide. The reaction vessel was immersed in a cold-water bath such that the temperature of the reaction mixture did not rise above 30°. (The bath was previously equilibrated as a closed system with a gas buret attached.) In some runs (with equivalent results), the reaction was carried out with a nitrogen sparge through ascarite. Gas evolution was immediately evident and after 5 hr amounted to 1500 ml. The mass spectrum of an aliquot of the condensible portion of this gas indicated that it was essentially pure carbon dioxide containing traces of solvent.

The acetonitrile and volatile components of the product mixture were removed by bulb-to-bulb distillation at room temperature and 1-mm pressure. Glpc analyses showed the presence and amounts of chloroform and carbon tetrachloride. The residue remaining after the bulb-to-bulb distillation was diluted with 10 ml of water, and steam distillation yielded 7.22 g of volatile residue after extraction with methylene chloride, drying, and evaporation of solvent. The nmr spectrum of this material indicated that it contained approximately equal amounts of pentachloroacetone (singlet at δ 6.91) and substituted pyridines (H-6 multiplet centered at δ 8.77). A number of smaller singlets at higher field (δ >6.8) were also present in the nmr spectrum of this mixture.

Treatment of an aliquot of this mixture with picric acid gave the equivalent of 0.27 g (0.69 mmol) of the picrate of γ-trichloromethylpyridine, mp 150–151° when mixed with authentic sample.

Distillation of the steam-volatile residue gave a fraction whose nmr spectrum was nearly free of pyridine protons, bp 65–85° (10 mm). Residistillation of this material gave a cut, bp 68.5° (8 mm), which showed an infrared spectrum in carbon tetrachloride which was identical with that of authentic pentachloroacetone. Its nmr spectrum showed a major singlet at δ 6.91, also identical with that of pentachloroacetone. However, there were two additional singlets at δ 6.63 and 6.13 which could be attributed to the tetrachloroacetone isomers.

The higher boiling fraction from the steam-volatile material was distilled at 54° (0.5 mm). On treatment with picric acid, the picrate of **1** was obtained, mp 150–152°, undepressed when mixed with authentic sample. Removal of the excess picric acid by extraction with bicarbonate gave a residue which showed infrared and nmr spectra identical with those of authentic **2**.

The residue after steam distillation was brought to pH 9 by the addition of potassium carbonate, extracted several times with methylene chloride, and dried. After removal of solvent the residue weighed 2.09 g. This material was chromatographed over Florosil. A fraction which was eluted by ether gave the picrate of γ-dichloromethylpyridine, mp 135–136°, undepressed when mixed with authentic sample. The nmr spectrum was also identical with that of the synthetic material. Other chromatography fractions gave nmr spectra similar to those of authentic α-dichloromethylpyridine, but the picrates from these fractions were those of the γ isomer, which crystallizes more readily. Fractions finally eluted with methanol–ethyl acetate were identical with authentic α-aminopyridine.

Registry No.—Pyridine N-oxide, 694-59-7; trichloroacetic anhydride, 4124-31-6; α-trichloroacetoxypyridine, 22796-45-8; **1**, 22796-40-3; **2**, 4377-37-1; **3**, 22796-42-5; **3** picrate, 22796-43-6; **4**, 4377-35-9.

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