ture boiling at 65–72° (2.5 mm). The mixture exhibited a gas chromatogram almost identical with that for the reaction product of **1a**, with slight differences in relative peak areas. The mixture gave tris(trimethylsilyl)methane with a small amount of an unidentified compound by methylation. The latter compound had OH absorption at 3400 cm^{-1} (silanol), being presumably $((CH_3)_3Si)_2CHSi(CH_3)_2OH$.

Aluminum Chloride Catalyzed Redistribution between 4 and 5.—In a 50-ml three-necked flask fitted with an air-tight stirrer, a calcium chloride tube, and a stopper, 2 g (0.0095 mol) of **4**, 2.5 g (0.0095 mol) of **5**, and 0.3 g of freshly sublimed aluminum were placed. The mixture was heated at 70–80° for 9 hr and was flash distilled to give 2.5 g of crystalline materials boiling at 70–115° (24 mm). The product was found to consist only of the same four components as those of the reaction mixture from **1a** or **1b**. The relative peak area of **4**:**6**:**7**:**5** (on silicone DC 550) was 1:9.3:11:2.4.

Preparation of (Chloromethyl)pentamethyldisilane.—To 3.0 g (0.43 g-atom) of dispersed lithium metal in 100 ml of dry ether was added 33 g (0.2 mol) of chloropentamethyldisilane in one portion at 0° under a nitrogen stream and then 25 g (0.19 mol) of bromochloromethane was added over a period of 30 min. After the addition was complete, the mixture was stirred for 2 hr at 0°. The mixture was then kept at room temperature overnight and hydrolyzed with saturated ammonium chloride solution. After work-up, the mixture was fractionated to give 6 g (18%) of (chloromethyl)pentamethyldisilane, 12 g of bis(pentamethyldisilanyl) ether, and 7 ml of mixture containing bis(pentamethyldisilanyl)methane, decamethyltetrasilane, and other unidentified materials. The (chloromethyl)pentamethyldisilane thus obtained was identified by comparing its ir spectrum and gas chromatogram with those of authentic sample.

Preparation of 1-(Chloromethyl)heptamethyltrisilane.—By the same procedure as above, 12 g of a mixture containing mainly 1-(chloromethyl)heptamethyltrisilane was obtained from 2 g (0.28 g-atom) of lithium, 15 g (0.066 mol) of 1-chloroheptamethyltrisilane, and 40 g (0.3 mol) of bromochloromethane. Pure 1-(chloromethyl)heptamethyltrisilane was isolated from the mixture by preparative glpc.

Registry No.—**1**, 2344-80-1; **2**, 5181-46-4; **3**, 15816-06-5; **4**, 5926-38-5; **5**, 15816-03-2; **6**, 15816-04-3; **7**, 15816-05-4.

The Reactions of Trichloroacetyl Chloride with 2-Picoline N-Oxide and Pyridylcarbinols

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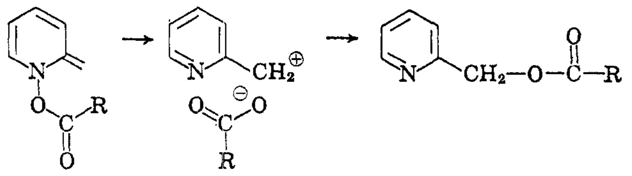
The reaction of trichloroacetyl chloride with 2-picoline N-oxide gives 2-pyridylmethyl chloride and carbon dioxide in high yields. This is shown to be a result of a reaction of the expected trichloroacetate ester with chloride ion. The formation of pyridyl chlorides from trichloroacetyl chloride and the corresponding alcohols is a general reaction.

The concerted decompositions of the *t*-butyl per esters of acids such as pivalic,[2,3] phenylacetic,[2-4] and trichloroacetic[2] seem to be well-established processes. If such behavior is general for any X–O bond homolysis, then the incorporation of such a structural feature into an acyloxy side chain should serve as a useful method for making the difficult choice between intramolecular radical-pair and ion-pair reactions. When the radical path is operative, nearly quantitative amounts of carbon dioxide should be obtained no matter how efficient the cage combination, which might explain the normal products, is proposed to be.

We have recently[5] applied this criterion to the cleavage of the –N–O– bond in the rearrangement of the anhydro bases thought to be involved in the reaction of 2-picoline N-oxide with acid anhydrides. The results of this study indicated that this cleavage was ionic since the carbon dioxide yields were not significantly increased on going from acetic to phenylacetic or trichloroacetic anhydride as reagent. During the course of these investigations we also examined the reaction of 2-picoline N-oxide with trichloroacetyl chloride. This reaction gave the qualitatively conflicting result that carbon dioxide is produced in high yield at a fairly rapid rate. We now wish to report the results of further studies of this reaction which indicate that trichloroacetate esters are susceptible to displacement by chloride ion under these relatively mild conditions.



Results and Discussion

When trichloroacetyl chloride is added into a refluxing chloroform solution of 2-picoline N-oxide (2 *M*), a rapid evolution of carbon dioxide (20% yield in 1 hr) occurs. The nmr spectrum of the solution after 1 hr shows the presence of the 2-picolylmethyl trichloroacetate ester (I) (singlet at 5.8 ppm) in about 40% yield. An additional singlet is also present at 5.1 ppm and continued reflux of the original solution leads to continued carbon dioxide formation and a decrease in the 5.8-ppm singlet accompanied by an increase in the 5.1-ppm peak. After a 12-hr reflux, the carbon dioxide yield is 83% and the trichloroacetate ester is nearly completely consumed. The nmr spectrum of the final solution indicated the new product to be present in 70% yield. The isolated yield of this compound is 30–40% after distillation. The product was identified as α-chloro-2-picoline (II) by its spectral properties, boiling point, and picrate.

The ester I, obtained in pure form from 2-pyridylcarbinol and trichloroacetic anhydride, gives II and carbon dioxide on treatment with hydrogen chloride, followed by reflux in chloroform or acetonitrile. When

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[1] Fellow of the Kosciusko Foundation on leave from Politechnika Wroclawska, Poland, 1966–1967.

[2] P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

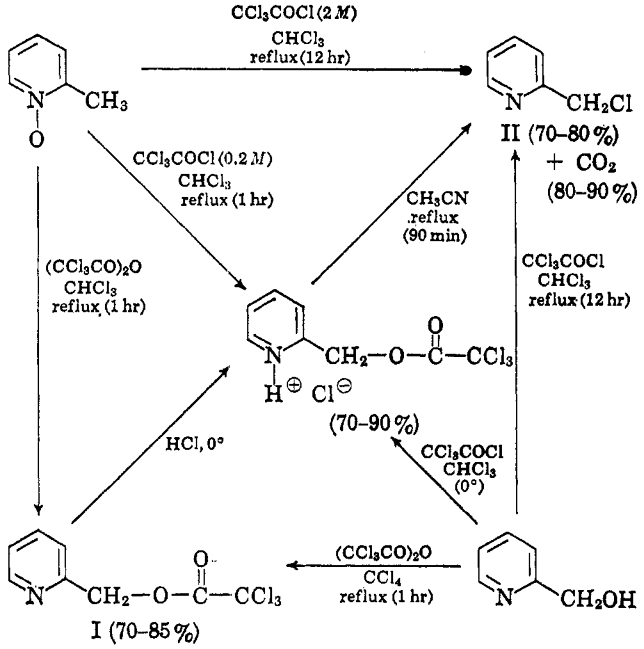
[3] T. Koenig and W. D. Brewer, *Tetrahedron Lett.*, 2773 (1965); T. Koenig and R. Wolf, *J. Amer. Chem. Soc.*, **89**, 2948 (1967).

[4] R. Neuman and J. Behar, *ibid.*, **89**, 4549 (1967).

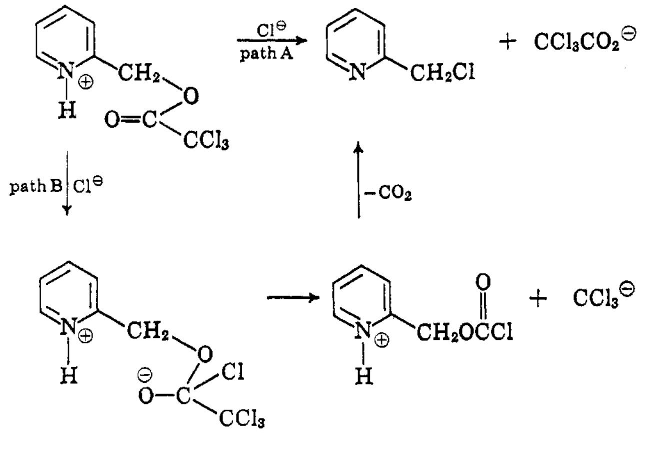
[5] T. Koenig, *ibid.*, **88**, 4045 (1966).

2-pyridylcarbinol is treated with trichloroacetyl chloride, in refluxing chloroform, II is again the product. These results are summarized in Scheme I.

SCHEME I



Two explanations for this rapid substitution process are readily apparent; direct displacement by chloride (path A), or attack of the chloride at the carbonyl followed by loss of the trichloromethyl anion (path B).



Initial control experiments indicated that the rate of decarboxylation of trichloroacetic acid was considerably slower in refluxing chloroform than the carbon dioxide formation in the N-oxide reaction (run 1, Table I).[6] This seemed to rule against path A. However, the trichloroacetate ester of phenol was found to be unreactive in the presence of pyridinum hydrochloride in boiling acetonitrile. This seems to rule against path B.

Reinvestigation of the decarboxylation of trichloroacetic acid with tertiary amines showed that the rates of these reactions depend on both the solvent and concentration (Table I). This is not due to a weak complex formation since the infrared spectrum of a 0.2 *M* solution of the acid and pyridine in chloroform shows no free pyridine to be present; a 10% excess of pyridine can be easily observed (ring band, 1570 cm^{-1}). This concentration dependence is in contrast to the first-order rates usually reported[7] for trichloroacetate salt decomposition.

TABLE I

RATES OF DECARBOXYLATION OF TRICHLOROACETIC ACID

Run	Solvent	Temp, °C	Base[a]	Concn, *M*	t/2,[b] min
1	$CHCl_3$	Reflux	Pyridine	0.2	720
2	$CHCl_3$	50	Pyridine	1.0	435
3	$CHCl_3$	51	Pyridine	2.0	173
4	$CHCl_3$	50	Triethylamine	1.0	200
5	CH_3CN	30	Pyridine	2.0	57
6	$(CH_3)_2SO$	30	Pyridine	1.0	18

[a] Amine-acid ratio, 1:1. [b] Time for one-half of the calculate amount of carbon dioxide to be evolved.

At high concentrations, the decarboxylation of trichloroacetic acid in the presence of amines is thus rapid enough to account for the observed behavior of the ester hydrochloride by path A though path B is not rigorously ruled out. When the N-oxide acid chloride reaction is carried out in dilute solution (0.2 *M*), the ester II is obtained in 65% yield even after reflux for 16 hr.

This substitution reaction with trichloroacetyl chloride also occurs with 3-pyridylcarbinol and 4-pyridylcarbinol and benzyl alcohol in the presence of pyridine. However, the 3- and 4-pyridylmethyl chlorides polymerized extensively to give mostly water-soluble tars. Picrates of the corresponding chlorides were obtained from the product mixtures after filtration of the tarry material. 2-Pyridylmethyl acetate does not react with chloride ion under these conditions.

These results indicate that trichloroacetyl chloride can act as a chlorinating agent in a fashion similar to thionyl chloride with added amines. The rapid rate of carbon dioxide formation by this complicated process makes the use of the trichloromethyl side chain a less unambiguous probe for radical *vs.* ionic cleavage of X–O bonds. The present results, however, finally serve to reinforce the previous conclusion that the reaction of picoline N-oxides with acid chlorides and anhydrides does not involve radical-pair intermediates.

Experimental Section

Infrared spectra were obtained using a Beckman IR-5 spectrophotometer. Nuclear magnetic resonance spectra are reported relative to tetramethylsilane, used as an internal standard, with a Varian A-60 spectrometer. All solvents were distilled before use. Trichloroacetic anhydride was obtained from K & K Laboratories and was distilled, bp 49° (0.5 mm). Trichloroacetyl chloride was obtained from the acid by the method of Bosshard.[8] All melting points and boiling points are uncorrected. Analyses were obtained from Berkeley Analytical Laboratories, Berkeley, Calif.

Pyridylmethyl Trichloroacetates.—In a typical run, trichloroacetic anhydride (33.3 g, 0.1 mol) was added to 100 ml of re-

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(6) The results of Table I are preliminary. A more complete account of the reaction of trichloroacetic acid with amines in these solvents will be published with data on the reaction of N-oxides with trichloroacetic anhydride in acetonitrile, which gives another variation of the expected behavior. Pyridine N-oxide does not react with trichloroacetic anhydride in refluxing chloroform but reacts rapidly in acetonitrile at 0–30°.

(7) L. Clark, *J. Phys. Chem.*, **63**, 99 (1959); G. Hall and F. Verhoek, *J. Amer. Chem. Soc.*, **69**, 613 (1947); L. Clark, *J. Phys. Chem.*, **64**, 1758 (1960); H. Patwardhan and A. N. Kappanna, *Z. Physik. Chem.* (Leipzig), **A166**, 51 (1933).

(8) H. Bosshard, R. Moroy, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 175 (1959).

TABLE II

ANALYTICAL DATA

Derivative	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % Cl	Calcd, % N	Found, % C	Found, % H	Found, % Cl	Found, % N
Trichloroacetate picrate		34.76	1.88	22.00	11.58				
2-ester	119–120.5					35.02	1.78	21.74	11.36
3-ester	141–143					35.08	1.64	21.76	11.32
Chloride picrate		40.41	2.54	9.94	15.71				
2-chloride	148–150[a]					40.57	2.39	10.03	15.52
3-chloride	129–131[b]					40.55	2.47	9.82	15.44
4-chloride	143–144[c]					40.60	2.37	10.15	15.42
4-Trichloroacetate HCl	126 dec	33.11	2.42	48.60	4.82	33.19	2.29	48.68	4.73

[a] Lit.[9] mp 152–153°. [b] T. Itai and H. Ogura [*J. Pharm. Soc., Japan*, **75,** 296 (1955)] give mp 130.5–132°. [c] H. Mosher and J. Tessieri [*J. Amer. Chem. Soc.*, **73,** 4925 (1951)] give mp 146–147°.

fluxing carbon tetrachloride containing 2-pyridylcarbinol (10.9 g, 0.1 mol). The resulting solution was cooled after 1 hr and neutralized with bicarbonate at 0°, dried, and distilled yielding the ester I as an unstable oil, bp 109–110° (0.5 mm). Its nmr spectrum in deuteriochloroform showed a singlet at 5.5 (two protons) and multiplets centered at 7.5 (three protons) and 8.6 ppm (one proton). Its infrared spectrum in carbon tetrachloride showed carbonyl absorption at 1755 cm^{-1}. A picrate was obtained (Table II), which could be recrystallized from benzene.

The procedure for the 3-pyridylmethyl trichloroacetate was identical. This compound, however, decomposed on attempted distillation. The nmr spectrum of the carbon tetrachloride solution after neutralization showed a singlet at 5.4 (two protons) and multiplets centered at 7.5 (two protons) and 8.4 ppm (two protons). Addition of a weighed amount of dioxane and integration of the nmr peaks indicated the ester was formed in 86% yield. The infrared spectrum of this solution showed carbonyl absorption at 1745 cm^{-1}. A picrate was obtained which was recrystallized from benzene (Table II).

In an identical experiment, a carbon tetrachloride solution of the 4-isomer was obtained (85% yield by nmr). This compound also decomposed on attempted distillation. A hydrochloride was obtained which was purified by sublimation (Table II).

2-Picoline N-Oxide and Trichloroacetyl Chloride.—Trichloroacetyl chloride (11 g, 0.066 mol) was added rapidly to a refluxing solution of chloroform (25 ml) containing freshly distilled 2-picoline N-oxide (5.45 g, 0.05 mol). The reaction was carried out in a closed system with a gas buret attached. Gas evolution was immediately observed and was followed as a function of time. After 21 hr, 1000 ml (80%) of gas had been evolved. The gas was identified as carbon dioxide in separate experiments by absorption on ascarite and by its mass spectrum.

Extraction of the product solution with cold bicarbonate followed by distillation gave a colorless oil [bp 75–77° (12 mm), 30–40% yield] which turned pink after a few minutes and solidified to a red solid after a few hours. The compound was identified as α-chloro-2-picoline (II) by its picrate (Table II) and its nmr spectrum which showed a singlet at 5.1 (two protons) and multiplets centered at 7.5 (three protons) and 8.6 ppm (one proton). The nmr spectrum after the bicarbonate wash indicated the chloride to be present in 70% yield using dioxane as an integration standard.

2-Pyridylmethyl Trichloroacetate Hydrochloride Reaction.—Dry hydrogen chloride gas was passed through a solution of the ester I (2.42 g, 0.01 mol) in acetonitrile at 0°. A white hydroscopic solid precipitated under these conditions and the infrared spectrum of this solid in chloroform showed carbonyl absorption at 1760 cm^{-1} and a broad absorption from 2000–2500 cm^{-1}. This material was refluxed in acetonitrile (0.02 *M*) for 3 hr giving 220 ml of gas and chloride II (75% yield by nmr; picrate, mp 150–151° undepressed).

Pyridylcarbinol–Trichloroacetyl Chloride Reactions.—In a typical run, trichloroacetyl chloride (2.31 g, 0.010 mol) was added to a refluxing solution of acetonitrile (50 ml) and 2-pyridylcarbinol (1.11 g, 0.01 mol) in a closed system with a gas buret attached. Gas evolution was immediately apparent and was 50% complete in 12 min. After 90 min, the evolved gas was 230 ml (92%) and refluxing was discontinued. The nmr spectrum of the resulting solution indicated that the chloride was present in 70% yield. A picrate was obtained (mp 148–150°, undepressed, Table II).

The procedure for the reaction with 3- and 4-pyridylcarbinols was identical. The gas evolution occurred at similar rates and to greater than 90% yield in both cases. The product solutions contained a large amount of solid, but picrates of the corresponding chlorides were obtained after filtration (Table II).

Rates of Trichloroacetic Acid Decarboxylation.—The rates of decarboxylation of trichloroacetic acid were determined in a fashion similar to the above procedures. Stirred solutions of the acid were equilibrated at the temperature of the run in a closed system with a gas buret attached. The amine was added rapidly and the volumes *vs.* time noted.

Registry No.—2-Picoline N-oxide, 931-19-1; trichloroacetyl chloride, 76-02-8; I, 15645-81-5; I (picrate), 15893-35-3; II, 4377-33-7; 3-pyridylmethyl trichloroacetate, 15645-81-5; 3-pyridylmethyl trichloroacetate picrate, 15645-49-5.

Acknowledgment.—This work was supported by a grant from the Public Health Service.