Kinetic Study on the Conversion of Pyridine- and Quinolinecarboxylic Acids to the Corresponding Trichloromethyl Compounds

Kazuyuki Takahashi, Koichi Takeda and Keiryo Mitsuhashi

Department of Chemistry, College of Technology, Seikei University, Musashino-shi, Tokyo, Japan 180

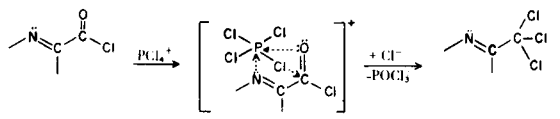
Received January 30, 1978

The reaction rates of the conversion of various substituted picolinic and quinaldinic acids to the corresponding trichloromethylpyridines and quinolines by treatment with phosphorus pentachloride in refluxing thionyl chloride have been measured, and the apparent second-order kinetic constants determined. The logarithmic rate constants (log k) were found to be linear with the basicities (p*K*a) of the unsaturated ring nitrogens in the substrates. The reaction constant, ρ, of the conversion was estimated.

J. Heterocyclic Chem., 15, 893 (1978)

Of the imidazole-, pyridine- and quinolinecarboxylic acids, the carboxyl group attached to the carbon atom α to the unsaturated ring nitrogen has been reported, in our previous papers (1,2), to convert to the trichloromethyl group by treatment with phosphorus pentachloride in excess thionyl chloride, and the reaction mechanism was proposed as in Figure I. In addition, influences of the

Figure I



basicity of the unsaturated ring nitrogen and of the steric factor on the conversion were roughly mentioned (3,4).

In the present work, the rate constants of the conversion for various substituted picolinic and quinaldinic acids were determined in order to clarify the effect of the basicity, quantitatively.

The reaction of the acid with phosphorus pentachloride was carried out in refluxing thionyl chloride, and at certain intervals the quantity of the resulting trichloromethyl compound in the reaction mixture was estimated by gas chromatography using an appropriate internal standard. The apparent second-order rate constants were obtained as a bimolecular reaction between the acid and phosphorus pentachloride. Thus obtained rate constants (k) are listed in Table I with the basicities (p*K*a) of the unsaturated ring nitrogen of each substrate, determined potentiometrically at 30°, and a plot of log k *versus* p*K*a is illustrated in Figure II.

Table I

Substrate	II (-COOH) p*K*a	II → III (-COOH → CCl_3) k (mol^{-1} sec^{-1})
a	4.93	1.20×10^{-4}
b	5.61	6.76×10^{-4}
c	5.09	2.04×10^{-4}
d	4.05	1.07×10^{-5}
e	4.69	8.91×10^{-6}
f	5.03	1.41×10^{-5}
g	3.56	1.86×10^{-6}
h	4.72	7.24×10^{-6}
i	4.74	8.51×10^{-6}
j	3.96	8.13×10^{-7}

Numbers and marks of compounds refer to those in Figure IV.

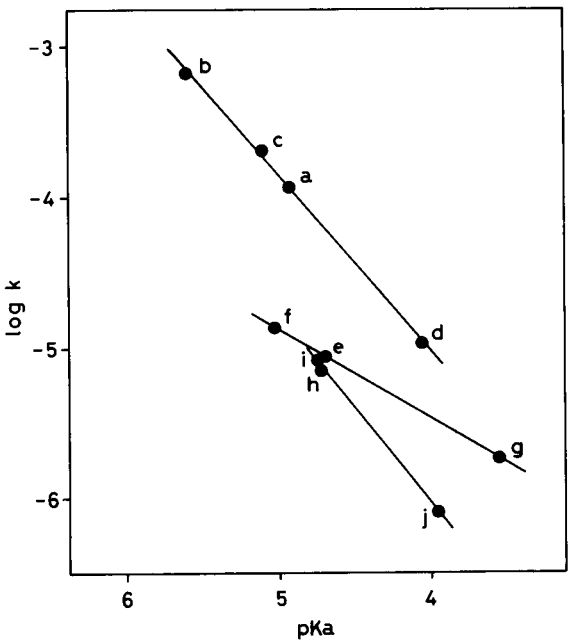


Figure II. Correlations between Logarithmic Rate Constants of the Conversion (II → III) and Basicities of Ring Nitrogen of II.

Figure II shows three different linear relations between log k and p*K*a; they are for (1) 4-substituted picolinic acids, (2) quinaldinic acids and (3) 3-methylpicolinic acids. This must indicate that log k depends linearly on p*K*a as far as the steric factor is similar.

Then, the Hammett rule was applied to these data in spite of insufficient number of substrates for each series. First, for 4-substituted picolinic acids, both log k and p*K*a are plotted *versus* Brown's σ_{para} of benzenoid substituent constant, respectively, in Figure III, which shows a good linearity. The fact that σ_{para} rather than σ_{meta} for the 4-substituent has a linear relation with log k suggests that the reaction site at the rate determining step of the conversion is the unsaturated ring nitrogen.

According to the Hammett equation, the reaction con-

Table II

Conditions of Gas Chromatography and Molar Sensitivity Ratios

Trichloromethyl Compounds	GC Condition (a) Column	Temp.	Internal Standard (b)	Molar Sensitivity Ratio ($-CCl_3$/Internal Standard)
IIIa	XE-60, 5%, 2 m	170°	A	0.744
IIIb	SE-30, 5%, 2 m	170°	A	0.91
IIIc	SE-30, 3%, 1 m	200°	B	0.934
IIId	SE-30, 3%, 1 m	170°	B	0.776
IIIe	SE-30, 5%, 2 m	170°	A	0.741
IIIf	SE-30, 5%, 2 m	200°	C	0.763
IIIg	SE-30, 5%, 2 m	200°	B	1.172
IIIh	SE-30, 5%, 1 m	170°	IIIi	1.056
IIIi	SE-30, 5%, 1 m	170°	B	0.948
IIIj	SE-30, 5%, 2 m	200°	B	0.784

(a) Carrier gas: He 30 ml./minute. (b) A: Benzotrichloride, B: Hexachloro-*m*-xylene, C: *p*-Chlorobenzotrichloride.

stant, ρ, was calculated as follows.

$$\rho_{conversion} = -4.52 \pm 0.11 \quad \underset{(II)}{-COOH} \rightarrow \underset{(III)}{CCl_3}$$

$$\rho_{dissociation} = 3.96 \pm 0.08 \quad \underset{(II)}{-N=} \rightleftharpoons \underset{+}{-\overset{H}{N}=}$$

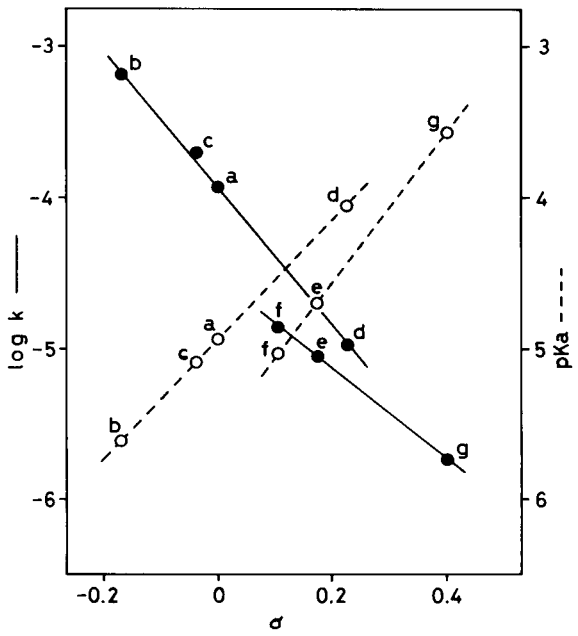


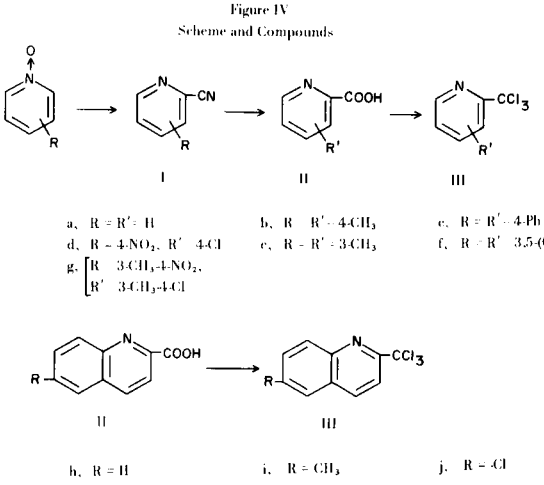
Figure III. Correlations of pKa and log k *vs.* σ.

Considering quinaldinic acids as benzo-substituted picolinic acids, then the Taft-Ingold equation, $\log (k/k_0) = \rho\sigma + E_s$, was applied since the hydrogen atom at the 8-position must have a steric effect to some extent. As the slope for quinaldinic acids is similar to that for 4-substituted picolinic acids as seen in Figures II and III, $\rho_{conv.}$ and $\rho_{diss.}$ obtained in the above for 4-substituted picolinic acids were used to calculate σ values and E_s for quinaldinic acids: benzo - (h) (σ = 0.136), 6-methylbenzo - (i) (σ = 0.125), 6-chlorobenzo - (j) (σ = 0.337); for the hydrogen atom at the 8-position, $E_s = -0.62 \pm 0.03$.

Next, for 3-methylpicolinic acids, the Taft-Ingold equation was applied to estimate $\rho'_{conv.}$, $\rho'_{diss.}$, $\sigma_{3\text{-}CH_3}$ and E_s on the basis of picolinic acid itself. The results are: $\rho'_{conv.} = -2.96 \pm 0.06$; $\rho'_{diss.} = 4.96 \pm 0.03$; $\sigma_{3\text{-}CH_3} = 0.174 \pm 0.001$; $E_s = -0.62 \pm 0.01$.

These ρ' values are somewhat different from the former ρ values and this might be due to the complex effect of 3-methyl group as deduced from the reaction mechanism. The values of $\sigma_{3\text{-}CH_3}$ and E_s are considered to indicate

Figure IV
Scheme and Compounds



the overall effect of the 3-methyl group on both 2-carboxyl group and 1-unsaturated ring nitrogen rather than the ordinary *ortho* effect.

EXPERIMENTAL

Synthetic routes and compounds are shown in Figure IV. Melting points are uncorrected. The nmr spectra were obtained using deuteriochloroform as a solvent and TMS as an internal reference.

Preparation of Substituted Picolinonitriles (I).

4-Methylpicolinonitrile (Ib).

A mixture of 10.9 g. (0.1 mole) of 4-methylpyridine *N*-oxide and 12.6 g. (0.1 mole) of dimethyl sulfate was heated at 70-80° for 5 hours. The mixture was then cooled and 20 g. of ice was added. Into the mixture, a solution of 7.2 g. (0.12 mole) of potassium cyanide in 40 ml. of water was added slowly at 0-10°. The mixture was kept standing overnight in an ice box, and the resulting precipitate was collected and recrystallized from *n*-hexane to give 4-methylpicolinonitrile (Ib), in a yield of 3.0 g. (25.4%), m.p. 87-88° (lit. (5) 88-89°); ir (potassium bromide): 2210 (s), 1590 (s), 1470 (m), 1380 (m), 1295 (s), 990 (s), 900 (s), 835 (s) cm^{-1}; nmr: σ 2.46 (s, 3H, $-CH_3$), σ 7.38 (q, 1H, 5-H), σ 7.54 (d, 1H, 3-H), σ 8.55 (d, 1H, 6-H), $J_{3,5}$ = 2 Hz, $J_{5,6}$ = 5 Hz.

Compounds Ic, Id, Ie, If and Ig were prepared by a similar method.

4-Phenylpicolinonitrile (Ic).

This compound was obtained in a yield of 2.0 g. (63.3%) from 3.0 g. of 4-phenylpyridine *N*-oxide, m.p. 98-99° (lit. (5) 99-100°); ir (potassium bromide): 2240 (m), 1595 (s), 1470 (m), 1395 (m), 870 (m), 850 (m), 765 (s), 695 (s) cm^{-1}; nmr: σ 7.5 (m, 5H, -Ph), σ 7.65 (q, 1H, 5-H), σ 7.85 (q, 1H, 3-H), σ 8.7 (q, 1H, 6-H), $J_{3,5}$ = 1.9 Hz, $J_{5,6}$ = 5.3 Hz, $J_{3,6}$ = 0.7 Hz.

4-Nitropicolinonitrile (Id).

This compound was obtained in a yield of 2.7 g. (50.7%) from 5.0 g. of 4-nitropyridine *N*-oxide, m.p. 72-73° (lit. (6) 73-74°); ir (potassium bromide): 2250 (m), 1560 (m), 1540 (s), 1460 (m), 1390 (s), 1360 (s), 1240 (m), 990 (m), 915 (m), 865 (m), 805 (s), 740 (m), 690 (m) cm^{-1}; nmr: σ 8.37 (q, 1H, 5-H), σ 8.52 (q, 1H, 3-H), σ 9.20 (q, 1H, 6-H), $J_{3,5}$ = 2 Hz, $J_{5,6}$ = 5 Hz, $J_{3,6}$ = 1 Hz.

3-Methylpicolinonitrile (Ie).

This compound was obtained in a yield of 9.5 g. (43.9%) from 20.0 g. of 3-methylpyridine *N*-oxide, m.p. 85-87° (lit. (7) 87-90°); ir (potassium bromide): 2230 (m), 1570 (s), 1450 (m), 1385 (m), 1115 (s), 1060 (m), 815 (s), 750 (m), 715 (m) cm^{-1}; nmr: σ 2.61 (s, 3H, $-CH_3$), σ 7.6 (q, 1H, 5-H), σ 7.9 (q, 1H, 4-H), σ 8.73 (q, 1H, 6-H), $J_{4,5}$ = 8.2 Hz, $J_{5,6}$ = 4.5 Hz, $J_{4,6}$ = 1.5 Hz.

3,5-Dimethylpicolinonitrile (If).

This compound was obtained in a yield of 6.5 g. (49.2%) from 12.3 g. of 3,5-dimethylpyridine *N*-oxide, m.p. 56-58°; ir (potassium bromide): 2200 (s), 1595 (m), 1560 (m), 1450 (broad), 1375 (m), 1265 (m), 1210 (s), 1130 (m), 895 (s), 750 (m), 720 (s) cm^{-1}; nmr: σ 2.42 (s, 3H, $-CH_3$), σ 2.54 (s, 3H, $-CH_3$), σ 7.43 (d, 1H, 4-H), σ 8.28 (d, 1H, 6-H), $J_{4,6}$ = 1Hz.

Anal. Calcd. for $C_8H_8N_2$: C, 72.73; H, 6.06; N, 21.21. Found: C, 72.95; H, 6.10; N, 20.92.

3-Methyl-4-nitropicolinonitrile (Ig).

This compound was obtained in a yield of 4.5 g. (56.7%) from 7.5 g. of 3-methyl-4-nitropyridine *N*-oxide, m.p. 62-63° (lit. (6) 64-65°); ir (potassium bromide): 2220 (w), 1590 (m), 1525 (s), 1445 (m), 1350 (s), 1300 (m), 1230 (m), 1165 (m), 1080 (m), 1030 (m), 870 (s), 765 (s), 750 (m), 735 (s) cm^{-1}; nmr: σ 2.8 (s, 3H, $-CH_3$), σ 7.92 (d, 1H, 5-H), σ 8.8 (d, 1H, 6-H), $J_{5,6}$ = 5.3 Hz.

Preparation of Substituted Picolinic Acids (II).

4-Methylpicolinic Acid (IIb).

Into 20 ml. of a 3*N* sodium hydroxide aqueous solution, 2.3 g. (0.02 mole) of Ib was added and the mixture was heated under reflux for 15 hours. The reaction mixture was then acidified to nearly *p*H 3 with 1*N* hydrochloric acid and the aqueous solution was evaporated to dryness. The residual solid was extracted with ethanol and the liquid was again evaporated to dryness. The resulting residue was recrystallized from benzene-*n*-hexane to give 4-methylpicolinic acid (IIb), in a yield of 1.67 g. (60.9%), m.p. 133-134°; ir (potassium bromide); 1645 (m), 1615 (m), 1590 (s), 1510 (m), 1460 (m), 1370 (s), 1340 (m), 1210 (s), 990 (m), 840 (m), 815 (m), 805 (m), 795 (s) cm^{-1}.

Anal. Calcd. for $C_7H_7NO_2$: C, 61.31; H, 5.11; N, 10.22. Found: C, 61.25; H, 5.32; N, 9.95.

Compounds IIc, IIe and IIf were prepared by a similar method.

4-Phenylpicolinic Acid (IIc).

This compound was obtained in a yield of 1.5 g. (75.4%) from 1.8 g. of Ic, m.p. 154-155°; ir (potassium bromide): 1650 (m), 1615 (s), 1460 (m), 1395 (s), 1350 (m), 1330 (m), 1235 (m), 1000 (m), 865 (m), 845 (m), 810 (m), 760 (s) cm^{-1}.

Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.36; H, 4.52; N, 7.04. Found: C, 72.61; H, 4.45; N, 6.88.

3-Methylpicolinic Acid (IIe).

This compound was obtained in a yield of 1.4 g. (60.3 %) from 2 g. of Ie, m.p. 117-118° (lit. (8) 118°); ir (potassium bromide): 1650 (s), 1595 (s), 1500 (s), 1360 (s), 1290 (m), 1225 (m), 1160 (m), 1065 (m), 850 (m), 805 (m) cm^{-1}.

3,5-Dimethylpicolinic Acid (IIf).

This compound was obtained in a yield of 2.1 g. (63.3 %) from 2.9 g. of If, m.p. 146-148°; ir (potassium bromide): 1890 (broad), 1700 (s), 1565 (m), 1435 (m), 1400 (m), 1385 (m), 1280 (s), 1235 (m), 1220 (m), 1100 (m), 1020 (m), 850 (m), 845 (m), 815 (m), 810 (m), 700 (s) cm^{-1}.

Anal. Calcd. for $C_8H_9NO_2$: C, 63.58; H, 5.96; N, 9.27. Found: C, 63.61; H, 6.02; N, 9.15.

4-Chloropicolinic Acid (IId).

According to the Matsumura's method (6), 0.7 g. (0.0047 mole) of Id was dissolved into 50 ml. of concentrated hydrochloric acid and the solution was heated under reflux for 7 hours. The reaction mixture was then evaporated to dryness, and the resulting residue was recrystallized from water to give 4-chloropicolinic acid (IId), in a yield of 0.3 g. (40.5%), m.p. 187-188° dec. (lit. (6) 186-187°); ir (potassium bromide): 1740 (broad), 1600 (m), 1580 (m), 1430 (m), 1320 (s), 1260 (m), 1200 (m), 1090 (m), 900 (m), 850 (m), 840 (s), 805 (m), 800 (m), 750 (m), 720 (s) cm^{-1}.

3-Methyl-4-chloropicolinic Acid (IIg).

This compound was prepared by a similar method to IId and obtained in a yield of 1.75 g. (41.6%) from 4 g. of Ig, m.p. 165-166° dec. (lit. (6) 163-164°); ir (potassium bromide): 1890 (broad), 1695 (s), 1560 (m), 1430 (m), 1400 (m), 1380 (m), 1275 (s), 1235 (m), 1220 (m), 1095 (m), 1015 (m), 850 (m), 815 (m), 810 (m), 700 (s) cm^{-1}.

Preparation of Substituted 2-Trichloromethylpyridines (III).

2-Trichloromethylpyridine (IIIa).

A solution of 2.2 g. (0.02 mole) of IIa and 12.5 g. (0.06 mole) of phosphorus pentachloride in 50 ml. of thionyl chloride was heated under reflux for 15 hours. The reaction mixture was then concentrated to *ca.* 15 ml., into which ice cubes and sodium carbonate were added, and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate and concentrated. The residual liquid was distilled under vacuum to give 2-trichloromethylpyridine (IIIa). The yield was 2.71 g. (69.0%), b.p. 91°/5 mm Hg (lit.(9) 125-126/25 mm Hg); ir (neat): 1585 (s), 1460 (s), 1430 (s), 1295 (m), 1200 (m), 1150 (m), 1100 (m), 1050 (m), 990 (m), 885 (s), 815 (s), 775 (m), 745 (s), 730 (s) cm^{-1}; nmr: σ 7.76 (m, 1H, 5-H), σ 8.19 (m, 1H, 3-H), σ 8.41 (m, 1H, 4-H), σ 9.16 (m, 1H, 6-H), $J_{3,4}$ = 8 Hz, $J_{4,5}$ = 6 Hz, $J_{5,6}$ = 4.5 Hz, $J_{3,5}$ = 1.5 Hz, $J_{3,6}$ = 1 Hz, $J_{4,6}$ = 2 Hz.

Compounds IIIb, IIIc, IIId, IIIe, IIIf and IIIg were prepared by a similar method.

2-Trichloromethyl-4-methylpyridine (IIIb).

This compound was obtained in a yield of 1.1 g. (46.2%) from 1.55 g. of IIb after the reaction for 30 minutes, b.p. 118-120°/18 mm Hg; ir (neat): 1600 (s), 1160 (w), 995 (w), 950 (w), 835 (m), 780 (s), 730 (m) cm^{-1}; nmr: σ 2.50 (s, 3H, -CH_3), σ 7.40 (q, 1H, 5-H), σ 8.07 (q, 1H, 3-H), σ 8.82 (q, 1H, 6-H), $J_{3,5}$ = 1.5 Hz, $J_{5,6}$ = 4.5 Hz, $J_{3,6}$ = 1 Hz.

Anal. Calcd. for $C_7H_6Cl_3N$: C, 39.90; H, 2.85; N, 6.65; Cl, 50.59. Found: C, 39.50; H, 2.50; N, 6.29; Cl, 50.48.

2-Trichloromethyl-4-phenylpyridine (IIIc).

This compound was obtained in a yield of 0.5 g. (36.5%) from 1.0 g. of IIc after the reaction for 15 hours, m.p. 66-67° (recrystallization from *n*-hexane); ir (potassium bromide): 1595 (s), 1545 (m), 1465 (m), 1395 (m), 820 (s), 775 (s), 760 (s), 745 (m), 730 (s), 700 (m) cm^{-1}; nmr: σ 7.45-7.9 (m, 6H, -Ph and 5-H), σ 8.3 (m, 1H, 3-H), σ 8.82 (m, 1H, 6-H), $J_{3,5}$ and $J_{3,6}$ were unable to estimate. $J_{5,6}$ = 5 Hz.

Anal. Calcd. for $C_{12}H_8Cl_3N$: C, 52.84; H, 2.94; N, 5.14; Cl, 39.08. Found: C, 52.61; H, 2.89; N, 5.43; Cl, 39.30.

2-Trichloromethyl-4-chloropyridine (IIId).

This compound was obtained in a yield of 0.8 g. (68.2%) from 0.8 g. of IId after the reaction for 20 hours, b.p. 129-130°/18 mm Hg; ir (neat): 1570 (s), 1400 (m), 1385 (m), 1205 (m), 930 (m), 830 (s), 780 (s), 720 (s) cm^{-1}; nmr: σ 7.62 (q, 1H, 5-H), σ 8.28 (d, 1H, 3-H), σ 8.90 (d, 1H, 6-H), $J_{3,5}$ = 2 Hz, $J_{5,6}$ = 5 Hz.

Anal. Calcd. for $C_6H_3Cl_4N$: C, 31.17; H, 1.30; N, 6.06; Cl, 61.47. Found: C, 31.16; H, 1.30; N, 6.36; Cl, 61.12.

2-Trichloromethyl-3-methylpyridine (IIIe).

This compound was obtained in a yield of 0.5 g. (40.7%) from 0.8 g. of IIe after the reaction for 15 hours, b.p. 133-134°/16 mm Hg; ir (neat): 1565 (w), 1450 (m), 1210 (w), 1120 (w), 890 (s), 8.20 (s), 780 (s), 710 (s) cm^{-1}; nmr: σ 2.78 (s, 3H, -CH_3), σ 7.37 (q, 1H, 5-H), σ 7.74 (q, 1H, 4-H), σ 8.53 (q, 1H, 6-H), $J_{4,5}$ = 7 Hz, $J_{5,6}$ = 4.5 Hz, $J_{4,6}$ = 1.5 Hz.

Anal. Calcd. for $C_7H_6Cl_3N$: C, 39.90; H, 2.85; N, 6.65; Cl, 50.59. Found: C, 39.71; H, 2.79; N, 6.35; Cl, 50.63.

2-Trichloromethyl-3,5-dimethylpyridine (IIIf).

This compound was obtained in a yield of 2.0 g. (89.1%) from 1.51 g. of IIf after the reaction for 30 hours, b.p. 150-153°/16 mm Hg; ir (neat): 1375 (w), 1210 (w), 1195 (w), 965 (w), 840 (s), 805 (s), 780 (s), 710 (s) cm^{-1}; nmr: σ 2.32 (s, 3H, 5-CH_3), σ 2.70 (s, 3H, 3-CH_3), σ 7.45 (d, 1H, 4-H), σ 8.23 (d, 1H, 6-H), $J_{4,6}$ = 1.5 Hz.

Anal. Calcd. for $C_8H_8Cl_3N$: C, 42.76; H, 3.56; N, 6.24; Cl, 47.44. Found: C, 42.60; H, 3.61; N, 6.07; Cl, 47.34.

2-Trichloromethyl-3-methyl-4-chloropyridine (IIIg).

This compound was obtained in a yield of 0.37 g. (43.2%) from 0.6 g. of IIg after the reaction for 50 hours, m.p. 64-66° (recrystallization from *n*-hexane); ir (potassium bromide): 1560 (m), 1450 (m), 1380 (m), 1260 (m), 1150 (m), 1020 (m), 895 (m), 845 (m), 810 (s), 785 (s), 725 (s), 700 (s) cm^{-1}; nmr: σ 2.8 (s, 3H, -CH_3), σ 7.43 (d, 1H, 5-H), σ 8.33 (d, 1H, 6-H), $J_{5,6}$ = 5 Hz.

Anal. Calcd. for $C_7H_5Cl_4N$: C, 34.29; H, 2.04; N, 5.71; Cl, 57.96. Found: C, 34.58; H, 2.29; N, 5.45; Cl, 58.10.

Compounds IIIh, IIIi and IIIj were already described in a previous paper (4).

Measurement of the Reaction Rates of the Conversion.

A solution of 2.5 mmoles of the carboxylic acid, 0.2 g. of the internal standard and 23 ml. of thionyl chloride was heated under reflux for 5 hours. Then, 3.12 g. (0.015 mole) of phosphorus pentachloride was added and heating was continued. At a certain interval after the addition, each one ml. portion of the reaction mixture was sampled. The sample was poured into a small amount of ice water, an aqueous solution of sodium hydroxide was added to alkaline, and the resulting mixture was extracted with dichloromethane. The extracted layer was dried over anhydrous sodium sulfate and concentrated to *ca.* one ml. Thus treated sample was subjected to gas chromatography to determine the resulting trichloromethyl compound quantitatively.

The conditions of gas chromatography, the internal standard and the molar sensitivity ratio are listed in Table II.

REFERENCES AND NOTES

(1) K. Mitsuhashi, K. Takahashi, T. Zaima and T. Asahara, *Kogyo Kagaku Zasshi*, **74**, 316 (1971).

(2) K. Takahashi, K. Mitsuhashi and T. Zaima, *Nippon Kagaku Kaishi*, 996 (1973).

(3) K. Takahashi, I. Kimura, Y. Takei, T. Zaima and K. Mitsuhashi, *ibid.*, 1530 (1975).

(4) K. Takahashi and K. Mitsuhashi, *J. Heterocyclic Chem.*, **14**, 881 (1977).

(5) F. H. Case and T. J. Kasper, *J. Am. Chem. Soc.*, **78**, 5842 (1956).

(6) E. Matsumura, M. Ariga and T. Ohfuji, *Bull. Chem. Soc. Japan*, **43**, 3210 (1970).

(7) W. E. Feely and E. M. Beavers, *J. Am. Chem. Soc.*, **81**, 4004 (1959).

(8) W. Mathes and W. Sauermich, *Chem. Ber.*, **90**, 758 (1957).

(9) E. T. McBee, H. B. Hass and E. M. Hodnett, *Ind. Eng. Chem.*, **39**, 389 (1947).