Both *6* and *7* are reduced as compared to *o*-nitrosobenzaldehyde and *o*-hydroxylaminobenzoic acid. An oxidised compound, azoxybenzene-*o*,*o*'-dicarboxylic acid was formed by the reaction of these substances. This compound was also formed in the reaction of *o*-nitrobenzyl alcohol.[1]

These results are thus in agreement with the hypothesis advanced earlier, that *o*-nitrosobenzaldehyde is an intermediate in the reaction of *o*-nitrobenzyl alcohol under acidic conditions.[1]

Experimental. *o*-Nitrosobenzaldehyde was prepared as described earlier.[3] Agnotobenzaldehyde (*2* or *3*) (m.p. 99–99.5 °C) had IR (KBr): 3300, 1610, 1530, 1355 cm^{-1}; IR (acetonitrile): 3400, 1710, 1670, 1610, 1540, 1350 cm^{-1}; NMR (d_6-acetone): δ 10.4 (s), 9.9 (s), 7–8 (m). *4* (m.p. 126.5–127 °C) had IR (KBr): 3320, 1650, 1440 cm^{-1}; NMR (d_6-acetone): δ 7–8 (4 H, m), 6.65 and 6.55 (2 H, AB, J_{AB} = 9Hz), 2.22 (3 H, s). The AB pattern collapsed to singlet (δ 6.65, 1 H) on D_2O addition. MS: *m/e* 179 ($C_9H_9NO_3$). *o*-Nitrosobenzaldehyde (m.p. 111–112 °C) had IR (KBr): 1700, 1610, 1270 cm^{-1} (*trans*-azo dioxide);[6,7] IR ($CHCl_3$): 1700, 1510, 1490 cm^{-1} (nitroso monomer); NMR ($CDCl_3$): δ 12.1 (1 H, s), 8.3–7.5 (3 H, m), 6.5 (1 H, d, J = 8Hz); MS: *m/e* 135 ($C_7H_5NO_2$).[4] Electronic spectrum ($CHCl_3$): λ_{max}: 780 nm (3.72 m^2 mol^{-1}).[8] The reactions of *o*-nitrosobenzaldehyde were performed as described for *o*-nitrobenzyl alcohol.[1]

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Synthesis of Some Substituted Picolinimidoyl Chloride Hydrochlorides

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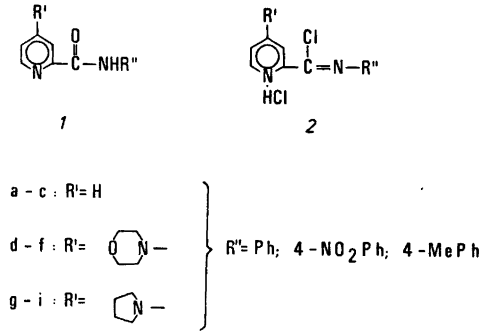
Imidoyl chlorides are useful as reactive intermediates, and our intention is to use some 4-amino substituted picolinimidoyl chlorides as such for studies on unsymmetrical imides. Even though a large variety of imidoyl chlorides are known,[1] the only picolinimidoyl chloride which has been reported [2] is *N*-phenylpicolinimidoyl chloride hydrochloride. This compound was prepared by Beckmann rearrangement of 2-pyridyl phenyl ketone. However, chlorination of amides is the most widely used method for preparing imidoyl chlorides, and the best known reagents are phosphorus(V) chloride (PPC), carbonyl dichloride, thionyl chloride (TC) or a combination of triphenylphosphine and tetrachloromethane.[3]

Preliminary experiments with some picolinamides showed that these compounds were resistant to chlorination by TC, the reagent of greatest convenience. They also gave addition complexes with other chlorinating agents, *e.g.* with triphenylphosphine and tetrachloromethane.



Scheme 1.

We here show that the series of picolinamides *1* can be converted to the corresponding picolinimidoyl chloride hydrochlorides *2*, *cf.* Scheme *1*, by using different combinations of chlorinating agents and different reaction temperatures and reaction periods.

Results. We have prepared the nine picolinamides *1a–i* (Table 1) from the corresponding

picolinoyl chloride hydrochlorides and amines. These amides were reacted either with TC, with a combination of TC and PPC, or with PPC and tetrachloroethane (Table 2) to form the corresponding picolinimidoyl chloride hydrochlorides *2a–i* (Table 3).

Experimental. General. IR spectra were recorded on a Perkin Elmer 254 grating spectrometer. Mass spectra were obtained on an AEI MS902 spectrometer with 70 eV bombarding electron energy. ^{1}H NMR spectra were obtained at 100 MHz on a Jeol FX100 instrument. All melting points are uncorrected and were obtained on a Büchi "Tottoli" melting point apparatus. Elemental analyses were carried out at Galbraith Laboratories, USA. Only A.R. grade solvents were used and all of the solvents which were used for the preparations of imidoyl chloride hydrochlorides were dried over molecular sieves, 3 Å.

4-(4-Morpholinyl)picolinic acid. A solution of 5.2 g (0.03 mol) of methyl 4-chloropicolinate [4] in 8 g (0.09 mol) of morpholine was heated under reflux for 48 h. After addition of 40 ml (0.09 mol) of 8 % aqueous hydrochloric acid, heating was continued at 100–105 °C for 48 h. The crystals which separated upon cooling in ice were filtered and gave 5 g (68 %) of 4-(4-morpholinyl)picolinic acid hydrochloride, m.p. 232–234 °C dec. The product was dissolved in boiling water, pH of the solution was adjusted to 5 and the crystals which separated upon cooling were recrystallized from methanol to give 4-(4-morpholinyl)picolinic acid, m.p. 254–255 °C dec. Mol. wt., obs. 208.0855, calc. for $C_{10}H_{12}N_2O_3$ 208.0848; *m/e* (% rel. int.): 164 (100, M – CO_2).

4-(1-Pyrrolidinyl)picolinic acid. A solution of 26 g (0.15 mol) of methyl 4-chloropicolinate [4] in 32 g (0.45 mol) of pyrrolidine was heated under reflux for 2 h and at 60 °C for 60 h. After addition of 120 ml (0.3 mol) of 9 % aqueous hydrochloric acid, heating was continued at 90–100 °C for 60 h. A yield of 18.9 g (55 %), m.p. 238 °C dec. of 4-(1-pyrrolidinyl)-picolinic acid was obtained upon cooling. The acid was recrystallized from methanol, m.p. 263–264 °C dec. Mol. wt., obs. 192.0886, calc. for $C_{10}H_{12}N_2O_2$ 192.0899; *m/e* (% rel.int.): 148 (100, M – CO_2).

Picolinamides 1a–i *(Table 1).* A solution of the picolinic acid (0.03 mol) in 20 ml (0.28 mol) of TC was heated under reflux for 1 h. After removal of excess TC, 30 ml of dry benzene was added and the hydrochloride of the picolinoyl chloride was filtered. This product was immediately suspended in 100 ml of dry benzene and heated under reflux with the amine (33 mmol) and 10 ml (0.13 mol) of pyridine. Removal of the benzene under reduced pressure gave a solid which was triturated with 100 ml of water. The acidity of the suspension was adjusted to about pH 8 with 10 % aqueous potassium hydroxide when necessary. The amide was filtered and recrystallized.

Table 2. Reactions of picolinamides with chlorinating agents.

Compound	Reaction with TC [a]			Reaction with TC and PPC [b]			Reaction with PPC and TCE [c]		
	Time, h	Temp. °C	Products	Time, h	Temp. °C	Products	Time, h	Temp. °C	Products
1a	4	20	*1a*+HCl, 94 %	3	20	*2a*, 74 %			
1b	4	80	*1b*+HCl, 79 %	3	80	*2b*, 79 %			
1c	2.5	20	*1c*+HCl, 79 %	0.2	70	*2c*, 72 %			
1d	3	80	*2d*+HCl, 75 %	3	80	*2d*+HCl, 75 %	5	100	*2d*, 76 %
1e	2.5	80	*1e*+HCl, 81 %	4	80	*1e*+HCl, 95 %	3	100	*2e*, 91 %
1f	3	80	*2f*+HCl, 70 %	66	70	*2f*+HCl, 81 %	4	100	*2f*, 68 %
1g	2	80	*2g*, 83 %	4	80	*2g*, 92 %			
1h	3	80	*1h*+HCl, 77 %	3	80	*2h*, 33 %	3	90	*2h*, 70 %
1i	3.5	80	*2i*, 75 %	3	80	*2i*, 89 %			

[a] Thionyl chloride. [b] Phosphorus(V) chloride. [c] Tetrachloroethane.

Table 1. Picolinamides.

Compound	Reaction time h	Yield %	M.p. °C	Formula	Mol. wt. Obs.	Mol. wt. Calc.	IR (Nujol) cm^{-1}
1a	1	70	75–76 [a]	$C_{12}H_{10}N_2O$			3340, 1670
1b	5	70	235–236 [b]	$C_{12}H_9N_3O_3$	243.0646	243.0644	3330, 1690
1c	3	70	98–100 [c]	$C_{13}H_8N_2O$			3340, 1675
1d	30	90	141–142	$C_{16}H_{17}N_3O_2$	[d]		3330, 1675
1e	60	87	285–287	$C_{16}H_{16}N_4O_4$	[d]		3320, 1695
1f	60	74	189–190	$C_{17}H_{19}N_3O_2$	297.1478	297.1477	3310, 1675
1g	2	84	191–193	$C_{16}H_{17}N_3O$	[d]		3290, 1675
1h	60	90	220–221	$C_{16}H_{16}N_4O_3$	[d]		3330, 1700
1i	60	94	205–207	$C_{17}H_{19}N_3O$	281.1527	281.1528	3300, 1680

[a] *Cf.* Ref. 2, m.p. 76–77 °C. [b] *Cf.* Ref. 6, m.p. 222–224 °C. [c] *Cf.* Ref. 7, m.p. 104 °C. [d] Anal. C, H, N.

Table 3. Picolinimodyl chloride hydrochlorides.

Compound	M.p. °C	Formula	Mol. wt.[a] Obs.	Mol. wt.[a] Calc.	IR (Nujol) cm^{-1}
2a	128–132 dec.	$C_{12}H_{10}Cl_2N_2$	216.0455	216.0455	1665
2b	171–175 dec.	$C_{12}H_9Cl_2N_3O_2$	261.0309	261.0306	1673
2c	148–152 dec.	$C_{13}H_{12}Cl_2N_2$	230.0608	230.0611	1660
2d	189–191 dec.	$C_{16}H_{17}Cl_2N_3O$	301.0978	301.0982	1630
2d + *x* HCl [b]	100–120 dec.	[c]			1635
2e	206–208 dec.	$C_{16}H_{16}Cl_2N_4O_3$			1640, 1665 (w)
2e–HCl	188 dec.	$C_{16}H_{15}ClN_4O_3$ [d]			1675
2f	167–172 dec.	$C_{17}H_{19}Cl_2N_3O$	315.1138	315.1139	1635
2f + *x* HCl [b]	82–95 dec.	[e,f]			1630
2g	212–215 dec.	$C_{16}H_{17}Cl_2N_3$	285.1030	285.1030	1640
2h	210–217 dec.	$C_{16}H_{16}Cl_2N_4O_2$			1640
2h–HCl	154–156 dec.	$C_{16}H_{15}ClN_4O_2$ [d]			1660
2i	211–214 dec.	$C_{17}H_{19}Cl_2N_3$	299.1189	299.1190	1640

[a] M–HCl, the highest *m/e* observed. [b] Negative test for sulfur, *cf.* Ref. 8. [c] Titration with sodium hydroxide gave eq.wt. of 145, calc. for *2d*, 169.5 and for *2d*+HCl, 125. [d] Anal. C, H, Cl, N. [e] Eq.wt. of 144, calc. for *2f*, 176.5 and for *2f*+HCl, 130. [f] ^{1}H NMR (CD_3OD): δ 2.4 (3 H, s) 3.86 (8 H, s), 7.11–7.40 (6 H, m), 7.80 (1 H, d, *J* 2.9 Hz) 8.20 (1 H, d, *J* 7.4 Hz). Corresponding values for *2f* · δ 2.38 (3 H, s), 3.86 (8 H, s), 7.14–7.37 (5 H, m), 7.70 (1 H, d, *J* 2.9 Hz), 8.23 (1 H, d, *J* 7.4 Hz).

Reactions of picolinamides with chlorinating agents (Table 2). The dry amide was weighed into a stoppered round-bottom flask and TC was added, or, PPC was weighed into the flask and the dry amide was added. The latter procedure was used when either TC or tetrachloroethane was to be added to the reaction mixture.

Dry benzene was added to the reaction products and volatile components were removed under reduced pressure. The picolinimidoyl chloride hydrochlorides (*2a–i*, Table 3) separated as bright yellow crystals upon addition of dry acetone and were stored over phosphorus(V) oxide. The reaction products were tested [5] for the presence of phosphorus.

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Electrohydrocyclodimerization of Dimethyl Benzene-1,2-diacrylate; Correction of the Structure of the Hydrocyclodimer

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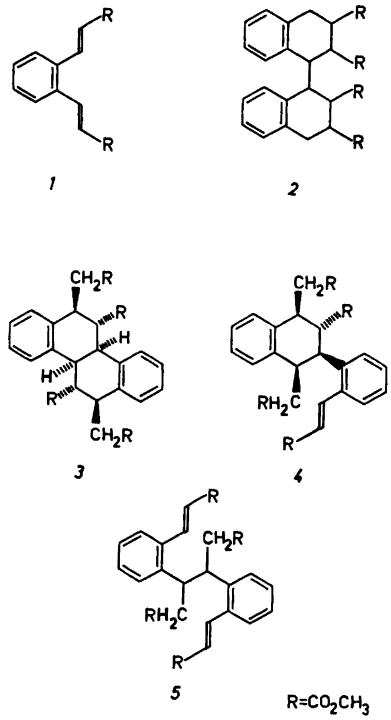
We have recently [1] commented upon the fact that the cathodic reduction of dimethyl benzene-1,2-diacrylate (*1*) seems to yield a single isomer of the hydrocyclodimer *2*, in spite of the fact that it, in principle, can exist in twenty isomeric forms (sixteen enantiomeric pairs and four *meso* forms). This prompted us to perform an X-ray crystallographic study [2] in order to establish the stereostructure of the hydrocyclodimer. It appeared that the previous structural assignment, based on NMR data, was wrong and that the correct structure is the even more interesting one of *3* (tetramethyl *cis* - 4b,5,6,10b,11,12 - hexahydrochrysene - *cis* - 5,11-carboxylate-6,12-diacetate) which is indeed not easily distinguishable from *2* on the basis of the usual array of spectroscopic techniques.



In the course of preparing crystals suitable for X-ray analysis two other hydrodimers (comprising 38 % of the total amount of hydrodimer; see Ref. 1) were isolated and subjected to an X-ray crystallographic study.[2] The one obtained from fractionated crystallization from ethyl acetate turned out to be *4* in which one ring closure has occurred whereas the one obtained from methanol had the structure of the simple hydrodimer, *5*, as the *meso* form.

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