ketone (2-adamantanone or 3-diamantanone) in dry ether at 0 °C was added dropwise 15 mmol of arylmagnesium bromide in ether. After the addition of Grignard reagent, the reaction mixture was stirred at room temperature for 1 h, followed by reflux for about 3 h. The reaction mixture on cooling was quenched in ice–water–HCl. Extraction into ether, drying over $MgSO_4$, and evaporation gave the tertiary alcohols in near-quantitative yields. Further purification of the alcohols was carried out on a silica gel column (ether as eluent). The purity of the alcohols was checked by GC and GC–MS.

General Method of Reduction of 2-Aryl-2-adamantyl (3-Aryl-3-diamantyl) Alcohols with $NaBH_4$. To a well-stirred mixture of 2-aryl-2-adamantanols or 3-aryl-3-diamantanols (10 mmol) and powdered $NaBH_4$ (10 mmol) in dry ether (20 mL) in a 100-mL round-bottom flask fitted with a reflux condenser was added dropwise triflic acid (50 mmol) at 0 °C over 10 min under dry nitrogen. After the addition, the reaction mixture was stirred for another $^1/_2$ h. It was then quenched in ice–water–bicarbonate. Extraction with ether, drying over $MgSO_4$, and solvent removal gave crude 2-aryladamantanes or 3-aryldiamantanes. Purification on a silica gel column (hexane as eluent) afforded pure hydrocarbon products, which subsequently were characterized by their ^{13}C NMR spectra, GC–MS, and elemental analysis.

2-Tolyladamantanes (isomeric): calcd C 90.20, H 9.80. Found: (ortho) C 90.41, H 9.86; (meta) C 90.28, H 9.80; (para) C 90.45, H 9.60.

3-Tolyldiamantanes (isomeric): calcd C 90.59, H 9.41. Found: (ortho) C 90.39, H 9.29; (meta) C 90.57, H 9.75; (para) C 90.63, H 9.57.

3-Phenyldiamantane: calcd C 90.85, H 9.15. Found: C 90.81, H 9.10.

General Method of Reduction with $HCO_2H–CF_3SO_3H$. To an ice-cold solution of 2-aryl-2-adamantanols or 3-aryl-3-diamantanols (10 mmol) in dry ether (20 mL) was added triflic acid (ca. 1–2 mmol), followed by dropwise addition of formic acid (96%, 12 mmol) over 10 min with stirring under dry nitrogen. The ice-cold bath was then removed, and the reaction was continued for another 5–10 min. It was then quenched in ice–bicarbonate and extracted with ether. The ethereal layer was dried over $MgSO_4$, filtered, and evaporated to give crude 2-aryladamantanes or 3-aryldiamantanes. Column chromatography on silica gel (hexane eluent) afforded pure hydrocarbon products.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. **1a**, 19066-24-1; **1a**-OH, 29480-18-0; **1b**, 115942-81-9; **1b**-OH, 115942-77-3; **1c**, 19214-04-1; **1c**-OH, 76481-45-3; **1d**, 19066-25-2; **1d**-OH, 29480-17-9; **2a**, 115942-82-0; **2a**-OH, 95531-42-3; **2b**, 115942-83-1; **2b**-OH, 115942-78-4; **2c**, 115942-84-2; **2c**-OH, 115942-79-5; **2d**, 115942-85-3; **2d**-OH, 115942-80-8; PhBr, 108-86-1; *o*-MeC_6H_4Br, 95-46-5; *m*-MeC_6H_4Br, 591-17-3; *p*-MeC_6H_4Br, 106-38-7; 2-adamantanone, 700-58-3; 3-diamantanone, 30545-23-4.

Hydrogen-Bonding Basicity of 1-Methyl-2-pyridone and of the Nitrogen Atom of Pyridine Derivatives toward Imides[1]

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We have previously studied equilibria in the hydrogen bonding of N–H acids, the only kind of acids involved in hydrogen bonding between the two strands of DNA, with monocoordinate oxygen bases, one of the two kinds of bases involved in such hydrogen bonding.[2] The bases studied were sulfoxides, a phosphoroxy base, and a saturated cyclic amide; we have now studied 1-methyl-2-pyridone, whose basic functional group is more nearly identical with those in DNA. We have also studied hydrogen bonding of N–H acids to the nitrogen atom of pyridine derivatives, the only other kind of hydrogen bonding holding the two strands of DNA together.

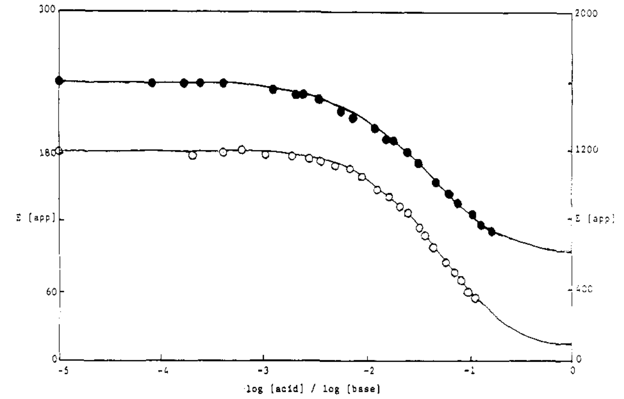

Figure 1. Plots of apparent extinction coefficients vs the logarithm of the concentration of the nonabsorbing reagent in the interaction of 2-methyl-2-ethylsuccinimide and 1-methyl-2-pyridone in carbon tetrachloride at 25 °C. Open circles are for the imide and refer to the scale on the left margin. Solid circles are for methylpyridone and refer to the scale on the right margin.

Experimental Section and Data Treatment

The 1-methyl-2-pyridone used was redistilled just before use to remove the pink color that is formed on standing. The sources and properties of the imides[2] and pyridines[3] have been described as have the techniques used for the UV and IR measurements and the methods used to calculate the equilibrium constants. Allowance was made for the dimerization of the imides and the further polymerization of 2-methyl-2-ethylsuccinimide.[2] In all cases the sum of the squares of the deviations from the observed absorbances was minimized except in the case of 2-aminopyridine where the sum of the squares of the deviations from the observed apparent extinction coefficients was minimized. The concentration of the absorbing reactant was changed, by no more than 55%, by addition of the other reactant, whose concentration ranged from zero to that required to give the maximum percent conversion listed in Table I. In all cases addition of the nonabsorbing reagent caused a decrease in the apparent extinction coefficient of the absorbing reagent at the wavelength at which measurements were made. The maximum absorbance was between 0.71 and 0.98.

Figure 1 contains plots of data on 2-methyl-2-ethylsuccinimide and 1-methyl-2-pyridone; both the UV and the IR data are plotted. As shown in Table I the K values differed by no more than 30%.

The thermodynamic pK_a of 1-pentyluracil was determined by potentiometric titration by using the Davies equation to calculate the effects of ionic strength.[4]

Results and Discussion

Figure 2, which is a plot of log K for hydrogen bonding to 1-methyl-2-pyridone vs the pK_a values for the imides, shows the expected tendency for the equilibrium constants to increase with increasing acidity of the acids involved. The points describe a straight line of slope (standard deviation) 0.342 (0.014). This is essentially the same as that of a similar plot for hydrogen bonding of *N*-methylpyrrolidone to about the same set of imides.[2] Thus the heteroaromatic amide 1-methyl-2-pyridone behaves in the same manner as a saturated amide. The line in Figure 2 would presumably be applicable to any imide if the steric conditions around the acidic hydrogen atom do not differ

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(1) This investigation was supported in part by Grant No. GM32784 from the National Institutes of Health.

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Table I. Hydrogen Bonding of 1-Methyl-2-pyridone with Imides in Carbon Tetrachloride at 25 °C[a]

imide	wavelength	ϵ_{react}, M^{-1} cm^{-1}	ϵ_{adduct}, M^{-1} cm^{-1}	max % conversion	$K(\sigma)$, M^{-1}	std dev in absorb.
2-methyl-2-ethylsuccinimide	337 nm	1680 (6)[b]	579 (18)	83	30.7 (1.7)	0.0074
	3403 cm^{-1}	256 (1)[c]	0 (3)	87	33.1 (1.3)	0.0057
1-pentyluracil	3392 cm^{-1}	201 (2)[c]	0[d]	82	12.1 (0.3)	0.016
2-chloro-3-methylmaleimide	337 nm	1459 (2)	127 (47)	47	83 (5)	0.0029
	3431 cm^{-1}	232 (3)	0[d]	90	98 (4)	0.018
2,3-dichloro-2-methylsuccinimide	337 nm	1717 (10)	49 (24)	83	299 (13)	0.012
	3392 cm^{-1}	189.0 (0.4)	0[d]	92	417 (4)	0.0040
tetrafluorosuccinimide	337 nm	1566 (2)	92 (6)	93	6890 (170)	0.0038
	3364 cm^{-1}	167 (1)	0[d]	97	9840 (1350)	0.016

[a] In carbon tetrachloride at 25 °C. The parenthesized figures are estimated standard deviations. [b] The reactant is 1-methyl-2-pyridone. [c] The reactant is the imide. [d] The least-squares value of this parameter was negative, and so the value 0 was assigned.

Table II. Equilibrium Constants for Hydrogen Bonding to 1-Methyl-2-pyridone[a] **and pK_a Values**[b] **for Imides**

imide	K[c]	pK_a[d]	dev of log K from least-sqrs line
1-pentyluracil	12.1	9.98[e]	0.09
2-methyl-2-ethylsuccinimide	32	9.34	0.12
2-chloro-3-methylmaleimide	91	7.54	0.04
2,3-dichloro-2-methylsuccinimide	390	5.84	0.01
tetrafluorosuccinimide	7200	2.1[f]	0.00

[a] In carbon tetrachloride at 25 °C. [b] In water at 25 °C. [c] Weighted average from the results in Table I. Weights inversely proportional to standard deviations. [d] From ref 2 unless otherwise noted. [e] Determined herein. [f] Estimated as described in ref 2.

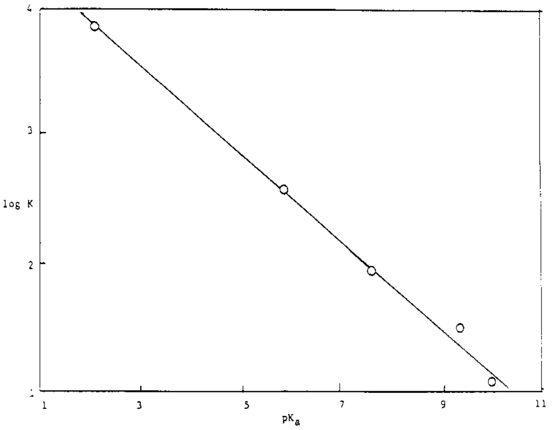

Figure 2. Plot of log K for hydrogen bonding of imides to 1-methyl-2-pyridone vs pK_a for the imides.

too much from those for the imides studied here.

Figure 3 is a plot of the log K values for hydrogen bonding to 2-methyl-2-ethylsuccinimide vs the pK_a values for the protonated forms of the pyridine derivatives. The points for pyridine and its 3- and 4-substituted derivatives describe a satisfactory line of slope 0.154 (0.007). The K values are each less than one-tenth those obtained with the same bases and hexafluoroisopropyl alcohol[3] although the acidity of the alcohol (pK_a = 9.3) is essentially the same as that of the imide (pK_a = 9.35) in water. The slope, 0.216 (0.009), is also larger in the case of the alcohol, as would be expected for a family of more strongly bonded complexes.

The K value for 2-aminopyridine is too large by 70% for its point to fall on the line described by the pyridines lacking 2-substituents, suggesting that the complex is partly doubly hydrogen bonded. The K value for 2-(dimethylamino)pyridine is too small by 5-fold and the value for 2-(diethylamino)pyridine too small by 7-fold to fall on this line. These deviations, presumably arising from steric hindrance, are somewhat smaller than those observed previously in hydrogen bonding of the same base to hexafluoroisopropyl alcohol.[3] Apparently the imide–pyridine complex does not exist to a major extent in a coplanar conformation.

The facts that the equilibrium constants are larger for hexafluoroisopropyl alcohol than for methylethylsuccinimide and larger for many of the oxygen bases, whose basicity is too weak to measure in aqueous solution, than for much more basic pyridines are illustrations of the generalization that the strength of hydrogen bonds in-

Table III. Hydrogen Bonding of 2-Methyl-2-ethylsuccinimide to Pyridine Derivatives[a]

base	wavelength	ϵ_{react}, M^{-1} cm^{-1}	ϵ_{adduct}, M^{-1} cm^{-1}	max % conversion	$K(\sigma)$, M^{-1}	std dev in absorb.
3-chloropyridine	3400 cm^{-1}	239 (1)[b]	0[c]	88	7.79 (0.07)	0.0040
	3400 cm^{-1}	239 (1)[b]	0[c]	90	7.50 (0.06)	0.0036
pyridine	3400 cm^{-1}	239 (0.4)[b]	12.5 (0.9)	96	17.4 (0.4)	0.0056
	3400 cm^{-1}	239 (1)[b]	11.6 (0.6)	95	18.7 (0.3)	0.0035
3-methylpyridine	3400 cm^{-1}	240 (1)[b]	5.4 (0.8)	95	22.0 (0.4)	0.0046
	3400 cm^{-1}	238 (1)[b]	7.9 (0.9)	95	23.6 (0.5)	0.0053
4-methylpyridine	3400 cm^{-1}	241 (1)[b]	8.2 (0.6)	95	24.1 (0.4)	0.0038
	3400 cm^{-1}	242 (1)[b]	7.8 (0.7)	94	23.9 (0.4)	0.0037
3,4-dimethylpyridine	3400 cm^{-1}	239 (1)[b]	7.5 (0.5)	95	26.3 (0.4)	0.0033
	3400 cm^{-1}	239 (1)[b]	9.1 (0.6)	94	27.5 (0.4)	0.0034
2-aminopyridine	290 nm	3775 (15)[d]	2685 (93)	88	59 (10)	18[e]
	313 nm	466 (32)[d]	3981 (262)	89	52 (7)	44[e]
2-(dimethylamino)pyridine	3400 cm^{-1}	239 (1)	0[c]	88	6.4 (0.1)	0.0032
	3400 cm^{-1}	238 (1)	0[c]	88	6.6 (0.1)	0.0065
2-(diethylamino)pyridine	3400 cm^{-1}	239 (1)	0[c]	83	5.5 (0.1)	0.0030
	3400 cm^{-1}	242 (1)	0[c]	83	4.6 (0.1)	0.0041

[a] In carbon tetrachloride at 25 °C. The parenthesized figures are estimated standard deviations. [b] The reactant is the imide. [c] The least-squares value of this parameter was negative, and so the value 0 was assigned. [d] The reactant is the pyridine. [e] Standard deviation in apparent extinction coefficients.

Table IV. Equilibrium Constants for Hydrogen Bonding by 2-Methyl-2-ethylsuccinimide to Pyridine Derivatives and pK_a Values for the Protonated Pyridines

base	pK_a[b]	K,[a] M^{-1}	dev of log K from least-sqrs line[c]
3-chloropyridine	2.81	7.6	0.001
pyridine	5.21	18	0.001
3-methylpyridine	5.70	23	0.027
4-methylpyridine	5.99	24	0.003
3,4-dimethylpyridine	6.48	27	0.023
2-aminopyridine	6.86	55	0.24
2-(dimethylamino)pyridine	6.99	6.5	0.72
2-(diethylamino)pyridine	7.22[d]	5.0	0.82

[a] Weighted average of values from Table III. Weights inversely proportional to standard deviations. [b] In water at 25 °C. From Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution: Supplement 1972*; Butterworth: London, 1972; unless otherwise indicated. [c] Through points for compounds lacking 2-substituents. [d] Reference 3.

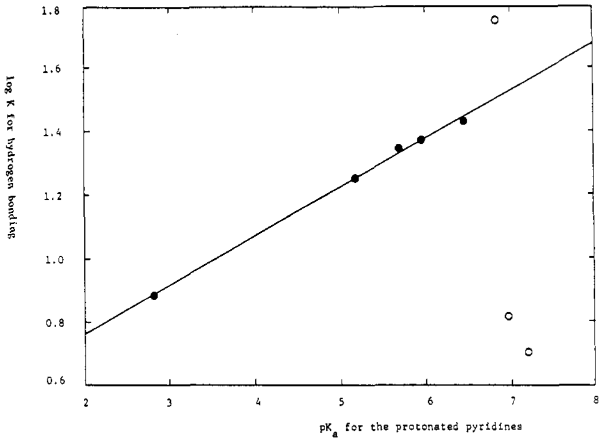

Figure 3. Plot of log K for hydrogen bonding of 2-methyl-2-ethylsuccinimide to pyridine derivatives vs pK_a for the protonated pyridines.

creases with increasing electronegativity of the atoms that are bonded when other factors are equal.[5]

Registry No. 1-Methyl-2-pyridone, 694-85-9; 2-methyl-2-ethylsuccinimide, 77-67-8; 1-pentyluracil, 13350-87-3; 2-chloro-3-methylmaleimide, 69636-50-6; 2,3-dichloro-2-methylsuccinimide, 69636-49-3; tetrafluorosuccinimide, 377-33-3; 3-chloropyridine, 626-60-8; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 3,4-dimethylpyridine, 583-58-4; 2-aminopyridine, 504-29-0; 2-(dimethylamino)pyridine, 5683-33-0; 2-(diethylamino)pyridine, 36075-06-6.

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Nickel Cyanide and Phase-Transfer-Catalyzed Carbonylation of Aryl Iodides in the Absence of Light

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Phase-transfer catalysis, widely used in organic chemistry,[2-4] is an area of considerable recent interest in organometallic chemistry and catalysis.[5] Much of the research in catalysis concerns carbonylation reactions, of which a significant proportion utilize halides as substrates. Both palladium[6] and cobalt [7,8] compounds are able to catalyze the conversion of benzyl halides to acids. Vinylic dibromides form mono acids[9] or diacids[10] in the presence of bis[1,2-bis(diphenylphosphino)ethane]palladium(0).

Table I. Nickel Cyanide and Phase-Transfer-Catalyzed Carbonylation of Aryl Iodides

substrate	reactn time, h	product	yield, % GC	yield, % isolated
C_6H_5I	16.5	C_6H_5COOH	95	80
4-$CH_3C_6H_4I$	16	4-$CH_3C_6H_4COOH$	90	65
3-$CH_3C_6H_4I$	16	3-$CH_3C_6H_4COOH$	55	45
2-$CH_3C_6H_4I$	17	2-$CH_3C_6H_4COOH$	99	80
4-ClC_6H_4I	16	4-ClC_6H_4COOH	68	60
4-$CH_3OC_6H_4I$	44	4-$CH_3OC_6H_4COOH$	48	40
2-$HOCH_2C_6H_4I$	17	2-$HOCH_2C_6H_4COOH$	100	60
1-$C_{10}H_7I$[a]	16	1-$C_{10}H_7COOH$	75	60
2-C_4H_3SI[b]	17	2-C_4H_3SCOOH	46	45

[a] 1-Iodonaphthalene. [b] 2-Iodothiophene.

One can effect the phase transfer, and sometimes biphasic, cobalt carbonyl catalyzed carbonylation of aryl halides to acids, *provided* the reaction mixture is subjected to irradiation at 350 nm (eq 1).[11] No reaction occurs in

$$\mathrm{ArX + CO \xrightarrow[(C_4H_9)_4N^+Br^-,\ h\nu\ (350\ mm)]{5N\ NaOH,\ C_6H_6,\ Co_2(CO)_8} ArCOOH} \qquad (1)$$

the dark. It is noteworthy that mono and double carbonylation occurs when ortho-halogenated benzoic acids are used as reactants.[12] An $S_{RN}1$ mechanism has been proposed for this reaction.

In 1985, one of us[13] described the use of cheap nickel cyanide as a catalyst for the carbonylation of allyl halides under phase-transfer conditions. We now report the first examples of the phase-transfer-catalyzed, direct carbonylation of aryl halides to acids under nonphotolytic conditions, using nickel cyanide as the metal catalyst.

Treatment of iodobenzene with carbon monoxide, sodium hydroxide (5 N), and toluene as the organic phase, cetyltrimethylammonium bromide as the phase-transfer catalyst, and nickel cyanide as the metal complex, at 90 °C and 1 atm for 16.5 h, afforded benzoic acid in 80% isolated yield (eq 2). The ratio of substrate to nickel

$$\mathrm{ArI + CO \xrightarrow[PhCH_3,\ C_{16}H_{33}N(CH_3)_3{}^+Br^-]{Ni(CN)_2\cdot 4H_2O,\ 5\ N\ NaOH} ArCOOH} \qquad (2)$$

catalyst was 10:1. This is a genuine phase-transfer reaction since iodobenzene is recovered unchanged in the absence of the quaternary ammonium salt. This reaction is sensitive to the base concentration since use of 1 N or 7.5 N sodium hydroxide affords a maximum of 20% benzoic acid. Nonpolar solvents [e.g., toluene] facilitate reaction while

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