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.

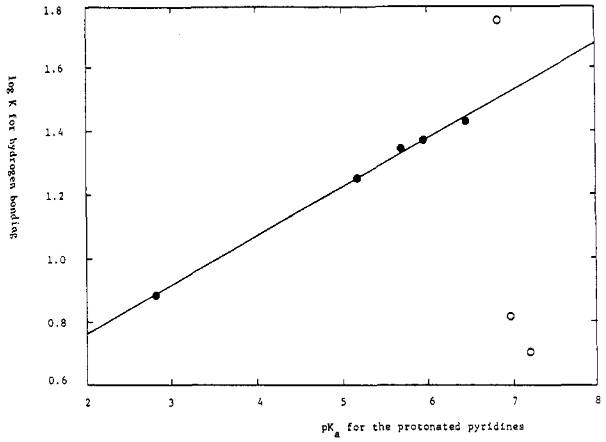

Figure 3. Plot of log K for hydrogen bonding of 2-methyl-2-ethylsuccinimide to pyridine derivatives vs pK_a for the protonated pyridines.

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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the use of a polar organic phase [e.g., 4-methyl-2-pentanone] results in very low conversions.

The carbonylation process is applicable to a variety of iodoarenes, affording acids in fair to very good yields. Chloro, methoxy, and hydroxymethyl substituents are unaffected, as well as the thiophene ring. The reaction times and product yields are listed in Table I. Bromobenzene does not react under the described conditions.

The carbonylation process may proceed by reaction of the in situ generated cyanotricarbonylnickelate ion[13] with the aryl iodide to give $ArNi(CO)_2CN$. The latter may arise by single electron transfer with intermediate formation of a radical pair within a solvent cage. Carbonylation of (σ-aryl)nickel (to the acylmetal complex), followed by carbon–nickel bond cleavage by base, would give the acid.

In conclusion, phase-transfer catalysis can be used, under nonphotolytic conditions, to carbonylate iodoarenes to carboxylic acids when nickel cyanide is employed as the metal catalyst. This method, which also avoids the use of nickel tetracarbonyl, is exceptionally simple in execution and workup of the reaction.

Experimental Section

General Data. See the same section in ref 13 for information on the use of instrumentation. The iodoarenes, hydrated nickel cyanide, and cetyltrimethylammonium bromide were commercial products and were used as received. Solvents were distilled prior to use.

General Procedure for the Phase-Transfer-Catalyzed Carbonylation of Aryl Iodides by Nickel Cyanide. A mixture of 5 N sodium hydroxide [20 mL), nickel cyanide [0.183 g, 1.0 mmol], aryl iodide [10 mmol], and cetyltrimethylammonium bromide [0.060 g, 0.16 mmol] in toluene (20 mL) was stirred under carbon monoxide at 90 °C [±5 °C, oil bath temperature]. After the reaction time indicated in Table I (reaction followed by gas chromatography), the layers were separated and crushed ice was added to the aqueous phase. The latter was then acidified with 10% HCl and extracted with ether or ethyl acetate (4 × 25 mL). The combined extracts were washed with water (25 mL), dried ($MgSO_4$), and evaporated, affording the acid. Characterization of the acid was made in comparison with properties (infrared, nuclear magnetic resonance, mass spectrometry) of authentic materials.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council and to British Petroleum for support of this research.

Registry No. $Ni(CN)_2$, 557-19-7; C_6H_5I, 591-50-4; 4-$CH_3C_6H_4I$, 624-31-7; 3-$CH_3C_6H_4I$, 625-95-6; 2-$CH_3C_6H_4I$, 615-37-2; 4-ClC_6H_4I, 637-87-6; 4-$CH_3OC_6H_4I$, 696-62-8; 2-$HOCH_2C_6H_4I$, 5159-41-1; 1-$C_{10}H_7I$, 90-14-2; 2-C_4H_3SI, 3437-95-4; C_6H_5COOH, 65-85-0; 4-$CH_3C_6H_4COOH$, 99-94-5; 3-$CH_3C_6H_4COOH$, 99-04-7; 2-$CH_3C_6H_4COOH$, 118-90-1; 4-ClC_6H_4COOH, 74-11-3; 4-$CH_3OC_6H_4COOH$, 100-09-4; 2-$HOCH_2C_6H_4COOH$, 612-20-4; 1-$C_{10}H_7COOH$, 86-55-5; 2-C_4H_3SCOOH, 527-72-0.

Kinetic Interpretation of Aromaticity: A Theoretical Study

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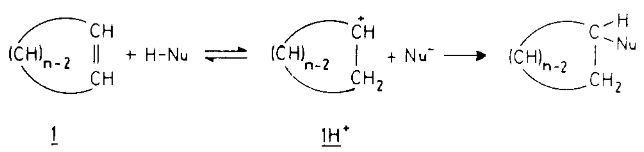
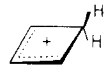
In spite of having been of great utility in the understanding of carbocyclic and heterocyclic chemistry, *aromaticity*, in our opinion, remains an ill-defined and unquantified concept with an unsatisfactory theoretical support. Definitions of aromaticity based on a purported thermodynamic "extra stability" are questionable; moreover, the quantum-mechanics foundations of this "extra stability" are unclear. In particular, recent theoretical studies of the electronic structure of benzene[2] have raised serious doubts about the current molecular-orbital interpretation of the benzene "extra stability" based on the π-electron delocalization.

Scheme I

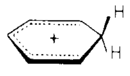


Tendency to react with "reversion to type", that is, regeneration of the aromatic ring, appears to be the most, if not the only, distincitive attribute of the peculiar chemical behavior of benzene and benzene-like (i.e., aromatic) species. Consider, for the sake of simplicity, the stepwise reaction between a cyclic conjugated polyene (1) and the conjugate acid (H–Nu) of a nucleophile (Nu) (Scheme I). It is well-known that after the first step, namely, the formation of the conjugate acid of the cyclic polyene ($1H^+$), two alternative reaction pathways are possible: (a) addition of Nu to $1H^+$ (nonaromatic behavior) and (b) abstraction of a proton from $1H^+$ by Nu ("reversion to type", aromatic behavior). Herein lies the difference between alkene addition and aromatic substitution.

Tendency to "revert to type" can be rationalized, in principle, on either a thermodynamic[3] or a kinetic basis.[4] Here we present a theoretical study of two possible pathways (i.e., the Nu addition to the *vicinal* position and the H^+ abstraction) for the model reaction of water, as a representative nucleophile, with the conjugate acid of two archetypal cyclic conjugated polyenes: cyclobutenylium ion ($2H^+$) and cyclohexadienylium ion ($3H^+$). The results lend computational support to a kinetic interpretation of the tendency to "revert to type" (aromatic behavior) shown by benzene after an electrophilic attack.



2H⁺



3H⁺

Computational Details

Due to the molecular size of the systems considered, the geometries of the transition structures for both the H_2O addition and H^+ abstraction reactions of $2H^+$ and $3H^+$ were calculated by using the MNDO SCF-MO model[5] as implemented in the MOPAC[6] program package. This model has proved effective in theoretical studies of the transition-state structures of numerous organic reactions, giving

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