these[10] and neutron-scattering experiments will be reported elsewhere.

Experimental Section

3-Chloro-2-butanone-d_7 (3). Biacetyl-d_6 was prepared via the acid-catalyzed exchange of biacetyl (Aldrich) and deuterium oxide.[11] After four cycles (0.7 N D_2SO_4/D_2O, 95 °C, 48 h per exchange), the distilled product was 99% deuteriated (99.5% by comparative ^1H NMR;[12] 98.9% by mass spectroscopy).

Perdeuteriobiacetyl (9.2 g, 0.1 mol) was reduced with zinc in D_2SO_4 according to the literature procedure for biacetyl.[13] When methylene chloride was used to extract the hydrophilic product, only seven extractions (total volume 350 mL) were required rather than the continuous extraction necessary with ether.[13] The solution was dried ($MgSO_4$), and the solvent was distilled at atmospheric pressure. The residue (6.6 g, 70%) was used directly in the next step.

The crude perdeuterioacetoin was dissolved in 10 mL of dry pentane and cooled to 0 °C. A 1:1 (molar ratio) mixture of chlorotrimethylsilane and pyridine (17.9 g, 0.095 mol) was added dropwise with stirring at 25 °C. The pyridine hydrochloride which formed was separated by centrifugation and washed with pentane. The combined pentane extracts were distilled at atmospheric pressure until the bath temperature reached 95–100 °C. The resulting trimethylsilyl ether was used without further purification.

The neat trimethylsilylacetoin was heated to 95 °C (bath temperature) and titrated with distilled thionyl chloride containing a few drops of pyridine. When 6 mL of thionyl chloride had been added, NMR spectroscopy (of the analogous reaction on protio material) indicated clean, quantitative conversion to chloro ketone. Attempts to isolate the chloro ketone quantitatively have failed for both protio and deuterio compounds. Thus the fraction boiling at 67 °C (200 mm; pure **3**) only amounted to 3.7 g (32.5% yield based on biacetyl, ~50% based on silylacetoin). This material was pure by GC/MS (parent peak m/e 113).

3-[(*N*,*N*-Dimethylselenocarbamyl)seleno]-2-butanone-d_7 (5). A solution of 9.9 mL of freshly distilled triethylamine in 250 mL of chloroform (dried over alumina) was cooled to −10 °C (ice–acetone), deoxygenated with argon, and treated for ca. 10 min with a fast stream of hydrogen selenide. *Complete exclusion of the ambient atmosphere is required throughout this entire sequence.* The hydrogen selenide stream was then replaced by a fast stream of argon. The argon was purged through the reaction mixture for 2 h at room temperature, or until no more H_2Se could be detected in the effluent gas (a trace of triethylamine will produce smoke if there is H_2Se present). In quick succession, 9.9 mL of triethylamine and 5.72 g of phosgeniminium chloride (Aldrich) were added to the previously cooled (0 °C) triethylammonium hydrogen selenide. The deep orange reaction mixture was allowed to stir at room temperature for 2 h. It was cooled to 0 °C and treated with a solution of 3.4 g of **3** in 10 mL of dry chloroform (dropwise) over 10 min. The mixture was stirred at room temperature for 2 h, the solvent was removed under vacuum overnight, and the residue was extracted with six 100-mL portions of ether. The ether was evaporated to afford a yellow oil which quickly crystallized. Diselenocarbamate **5** (6.4 g, 73% yield), pure by NMR and mass spectra, was thus obtained. This material was subjected to the usual TMTSF synthesis (see below) without further purification.

Perdeuteriotetramethyltetraselenafulvalene. The above diselenocarbamate was added over 10 min to stirred, cooled (−10 °C) D_2SO_4 (18 mL, 99% deuterated Aldrich). After the addition was complete, the mixture was heated to 58 °C (internal temperature) over 5 min and stirred at that temperature for another 5 min, cooled in ice–acetone, and poured onto ~50 g of ice. The mixture was filtered rapidly three times (until the filtrate remained clear) and then treated with a filtered solution of excess sodium hexafluorophosphate in 20 mL of water. The resulting precipitate was separated by suction filtration on a glass frit and was washed copiously with water. It was dissolved in methylene chloride, and the solution was dried (sodium sulfate) and evaporated to afford 5.9 g (64%) of tan salt **6**.

This solid was immediately suspended in 200 mL of 70% aqueous methanol, and the suspension was cooled to −10 °C while being degassed with argon over 15 min. Hydrogen selenide was then passed through the suspension at that temperature for 15 min, which caused the solid slowly to turn orange. The reaction mixture was stirred at room temperature for 2 h while excess hydrogen selenide was allowed to vent through two KOH traps. The product was filtered, washed with water, and dried by being dissolved in methylene chloride–benzene and treated with $MgSO_4$. Filtration followed by evaporation yielded 4.15 g (96%) of the deuterio selenone **7** as a red solid. Recrystallization via multiple extraction with hexane gave red needles: mp 150–151 °C; spectroscopic properties as shown in Table I; mass spectrum, parent ion at m/e 312.

A suspension of 2.6 g of **7** was refluxed in 7 mL of benzene under argon, and 1.9 mL of distilled trimethyl phosphite was added in a fine stream. The mixture was refluxed for 45 min, cooled, filtered, washed with ether, and dried under argon to obtain 1.72 g (90% yield) of purple prisms. Recrystallization from chloroform (≤50 mL) gave 1.57 g of small needles. Vacuum gradient sublimation onto Teflon at 10^{-5} torr and an initial temperature of 165 °C afforded material for electrochemical crystal growth. Spectroscopic properties are shown in Table I. Comparative NMR showed 99.5% deuteration.

Registry No. **2**, 79043-78-0; **3**, 79043-79-1; **4**, 79043-80-4; **5**, 79057-59-3; **6**, 79057-60-6; **7**, 79043-81-5; **7** dedeuterio, 53808-62-1; **8**, 79057-61-7; **8** dedeuterio, 55259-49-9; biacetyl, 431-03-8; perdeuteriobiacetyl, 22026-37-5; perdeuterioacetoin, 79043-82-6; triethylamine, 121-44-8; phosgeniminium chloride, 33842-02-3.

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(12) An NMR spectrum of a weighed sample of the deuterium-substituted compound was recorded and integrated; a small, carefully weighed sample of the proton-substituted sample was added, and the spectrum integrated. From the difference in the integral of the signal one could determine extent of deuteriation.

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Practical, Catalytic Synthesis of Anthranilic Acids

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This paper describes a convenient new route to the substituted anthranilic acids **3**. In order to meet our requirements for a technical synthesis of anthranilic acids, we considered use of nickel–[2] or palladium–phosphine complex[3] catalyzed carbonylations of 2-bromoanilines. We decided to investigate palladium catalysts, e.g., $Pd(PPh_3)_4$, $Pd(PPh_3)_2(Cl)_2$, etc., because these systems seemed to be more robust and easier to handle than the nickel analogues. Previous workers[4] had found that palladium–triphenylphosphine complex catalyzed substitution reactions of 2-bromoanilines gave poor results, apparently because of quarternization of triphenylphosphine by the substrate which gave the poor ligand $[Ar(NH_2)PPh_3]^+$. Two solutions to this problem, which were described by Heck,[5,6] are

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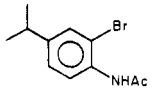
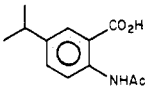
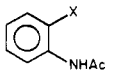
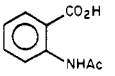
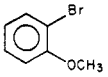
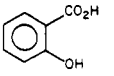
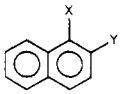
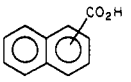
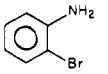
Table I. Anthranilic Acid Derivatives by Catalytic Carbonylation[a]

substrate			catalyst,	reaction	acids 2			acids 3		
no.	R_1	R_2	wt %	time,[b] h	no.	yield, %	mp, °C	no.	yield, %	mp, °C
1a	H	H	1.0	4	2a	75	183-185[c]			
1b	H	s-C_4H_9	1.0	18	2b	not isolated		3b	88	73-78[d]
1c	H	i-C_4H_9	1.0	18	2c	not isolated		3c	92	124-127[e]
1d	H	OCH_3	1.0	7	2d	30[f]	160-161	3d	46	145-148[g]
1e	i-C_3H_7	i-C_3H_7	1.0	16	2e	not isolated		3e	24	112-114
1f	H	i-C_3H_7	0.4	2.5	2f	85	167-170.5	3f	72	130-132
1f	H	i-C_3H_7	0.4	8	2f	94				
1f	H	i-C_3H_7	0.2	18	2f	not isolated		3f	75	
1f	H	i-C_3H_7	0.1	36	2f	not isolated		3f	79	
1f	H	i-C_3H_7	0.4[h]	8.5	2f	84				
1f	H	i-C_3H_7	0.4[i]	10	2f	79				

[a] All reactions were run in 1.1 equiv of tributylamine and 3 equiv of water at 110-125 °C under 2-3 atm of carbon monoxide. Catalyst was delivered as $Pd(PPh_3)_2(Cl)_2$ unless otherwise indicated, and an equal weight of triphenylphosphine was added. All yields refer to isolated yields. [b] For absorption of 1 equiv of carbon monoxide. All substrates were fully carbonated with the exception of 1e (~95% conversion). [c] Lit.[11] mp 185-186 °C. [d] Lit.[12] mp 79-80 °C. [e] Crystallized from methylene chloride-hexane. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.52; H, 7.79; N, 7.11. [f] Yield of analytical sample; the crude yield was 77%. [g] Lit.[13] mp 148-150 °C. [h] Catalyst precursor was $Pd(PPh_3)_2(Br)_2$. [i] Catalyst precursor was $Pd(PPh_3)_4$.

Table II. Palladium-Catalyzed Carbonylations of o-Bromoacetanilides and Related Substrates in Tri-n-butylamine-Water[a]

substrate	catalyst, wt %	reaction time, h	product	yield,[b] %	mp, °C
	0.4	2.5		85	167-170.5
					
X = Br	1.0	3.5		75	183-185
X = Cl	1.0	18	no reaction[c]	0	
	1.1	75		27	155-156.5
					
X = Br; Y = H	1.1	24	1-acid	48	159-161
Y = Br; X = H	1.1	69	2-acid	66	182-183.5
	5.0[d]	70	no reaction	0	

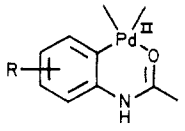
[a] General conditions: 3 atm of CO; 110-130 °C; Bu_3N (1.1 equiv); H_2O (ca. 3 equiv); $Pd(PPh_3)_2(Cl)_2$ + 2% PPh_3. [b] Recrystallized yields. [c] Catalyst precipitated. [d] Catalyst was $Pd(P(o\text{-}CH_3C_6H_4)_3)_2Cl_2$.

use of sterically hindered ligands [e.g., tris(2-tolyl)phosphine] in place of triphenylphosphine or use of expensive 2-iodoanilines as substrates. In the presence of iodide, phosphines are not needed to stabilize the palladium catalysts. Both approaches avoid loss of the catalyst, but rates remain slow and necessary catalyst loadings high. It occurred to us that for our purposes a better approach might be to carbonylate the corresponding acetanilides, 1. The $NHCOCH_3$ group is both larger and less strongly electron donating than the NH_2 group, and these factors were expected to make quaternization of phosphorus relatively less favorable. Accordingly, carbonylations of the 2-bromoacetanilides 1 were investigated. We were gratified to find that these substrates gave very fast rates and good yields in palladium-catalyzed carbonylations.

Our anthranilic acid synthesis is outlined in Scheme I, and the substituted anthranilic acids which have been prepared are shown in Table I. The carbonylation products are the *N*-acetylanthranilic acids 2, which are readily hydrolyzed in base to the corresponding anthranilic acids 3. When 3 is the desired product, the carbonylation reaction mixture is simply diluted with 1 N NaOH and heated overnight at 90 °C. It is also possible to isolate the acetanilides 2 by acidifying the carbonylation reaction mixture with hydrochloric acid and filtering off 2, which precipitates. When 2 is the desired product, long reaction times should be avoided because some hydrolysis of 2 to 3 may occur under the carbonylation conditions, and the presence of 3 interferes with the isolation and purification of 2.

The last six entries in Table I give data for carbonylations of 1f with various catalysts and catalyst loadings. Comparison of these results with those given in Table II for carbonylations of some other aryl halides suggests that 2-bromoacetanilides are strongly activated for palladium-catalyzed carbonylations. Assuming the mechanism of carbonylation to be given by eq 1, we suggest that oxidative addition of 1 to palladium(0) is favored by developing chelation of the acetyl ligand, leading to the stabilized intermediate 4.

$$ArBr + Pd^0 \xrightarrow{\text{oxidative addition}} ArPd^{II}X \rightleftharpoons^{CO} ArPd^{II}(CO)Br \rightarrow ArC(O)Br + Pd^0 \quad (1)$$



4

Support for this proposal is provided by the recent finding that acetanilide reacts stoichiometrically with $Pd(OAc)_2$ to give a dimeric complex formulated as two 4 units bridged by two acetates.[7] The intermediacy of a similar, intramolecular complexation has been proposed by Ban to account for the formation of cyclic imides from carboxamidoaryl bromides.[8]

Experimental Section

Tri-*n*-butylamine was stirred 18 h over KOH and then distilled under argon from sodium. Water was hydrogenated over Raney nickel.[9] Dichloro- and dibromobis(triphenylphosphine)palladium(II) and tetrakis(triphenylphosphine)palladium(0) were prepared by following the method of Hartley.[10]

***N*-[2-Bromo-4-(1-methylpropyl)phenyl]acetamide (1b)** was obtained as described below for **1f** from *N*-[4-(1-methylpropyl)phenyl]acetamide:[14] 72% yield; mp 90–92.5 °C (after recrystallization from ethanol–water).

Anal. Calcd for $C_{12}H_{16}BrNO$: C, 53.35; H, 5.97; N, 5.19; Br, 29.58. Found: C, 53.28; H, 5.94; N, 5.17; Br, 29.49.

***N*-[2-Bromo-4-(2-methylpropyl)phenyl]acetamide (1c)** was obtained as described below for **1f** from *N*-[4-(2-methylpropyl)phenyl]acetamide:[15] 83% yield; mp 104–106 °C (after recrystallization from ethanol–water).

Anal. Calcd for $C_{12}H_{16}BrNO$: C, 53.35; H, 5.97; N, 5.19; Br, 29.58. Found: C, 53.22; H, 6.02; N, 5.23; Br, 29.58.

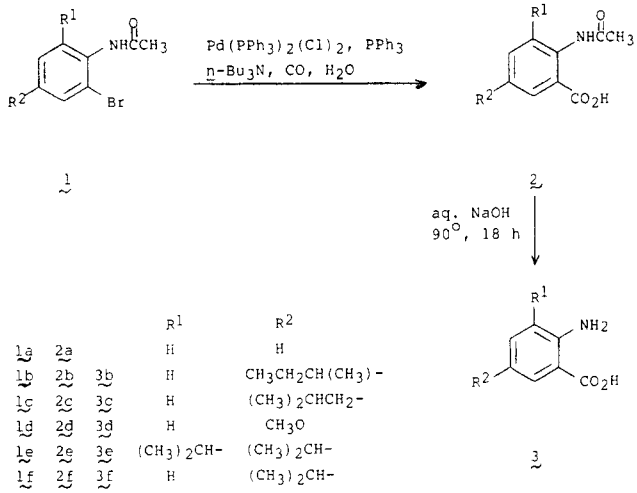
***N*-[2-Bromo-4,6-bis(1-methylethyl)phenyl]acetamide (1e).** To 30 g (0.17 mol) of 2,4-bis(1-methylethyl)aniline[16] in 100 mL of chloroform was added 10.8 mL (0.21 mol) of bromine in 30 mL of chloroform over the course of 2 h. The temperature varied during the addition between 16 and 24 °C. After a further 30 min, the reaction mixture was made basic with 3 N sodium hydroxide solution, the layers were separated, and the organic layer was washed with aqueous sodium sulfite, dried ($MgSO_4$), and concentrated to give 43 g (99%) of crude 2-bromo-4,6-bis(1-methylethyl)aniline which gave a molecular ion peak at m/e 255 in the mass spectrum.

A solution of 7.58 g (0.030 mol) of the crude bromoaniline in 15 mL of acetic anhydride and 7 mL of pyridine was stirred at room temperature for 24 h. The reaction mixture was made basic with saturated $NaHCO_3$ solution and was diluted with water. The oil which separated solidified on being allowed to stand and was crystallized from ethanol–water to give 5.75 g (65%) of **1e**, mp 103–106 °C.

Anal. Calcd for $C_{14}H_{20}BrNO$: C, 56.38; H, 6.76; N, 4.70; Br, 26.79. Found: C, 56.50; H, 6.92; N, 4.70; Br, 27.06.

***N*-[2-Bromo-4-(1-methylethyl)phenyl]acetamide (1f).** A solution of 100 g of "cumidine" obtained from Givandan Corp. [ca. 70% 4-(1-methylethyl)aniline and 30% of the corresponding ortho and meta isomers] and 300 mL of acetic acid was refluxed 3 h. The reaction mixture was concentrated under reduced pressure and then codistilled under reduced pressure with toluene (2 × 50 mL). The dark oily residue was diluted with 500 mL of hexane and heated on a steam bath. Ethyl acetate (ca. 10 mL) was added to effect solution. The crude product which precipitated on cooling was washed with hexane and then recrystallized from hexane (500 mL)–ethyl acetate (50 mL). A second crystallization, from hexane (400 mL)–ethyl acetate (100 mL) gave 61.1 g (47%) of 1-(acetylamino)-4-(1-methylethyl)benzene, mp 103–104 °C (lit.[17] mp 102 °C).

Scheme I



			R^1	R^2
1a	2a		H	H
1b	2b	3b	H	$CH_3CH_2CH(CH_3)$-
1c	2c	3c	H	$(CH_3)_2CHCH_2$-
1d	2d	3d	H	CH_3O
1e	2e	3e	$(CH_3)_2CH$-	$(CH_3)_2CH$-
1f	2f	3f	H	$(CH_3)_2CH$-

This material (61.1 g, 0.341 mol) was mixed with 400 mL of acetic acid and 40.0 g (0.41 mol) of anhydrous sodium acetate, and the mixture was shielded from light as 23.0 mL (0.45 mol) of bromine was added dropwise at a rate sufficient to maintain a reaction temperature of 40–50 °C. The addition took 30 min, and at the end of this period, the reaction was found to be complete by TLC (3:1 ether–hexane). Salts were removed by filtration, and the filter cake was washed with dichloromethane (100 mL). Concentration under reduced pressure gave the crude bromide as a yellow solid. This was dissolved in 600 mL of boiling 50% aqueous ethanol, and 125 mL of water was added to the boiling solution while a continuous stream of argon was passed through the solution. The sealed flask was then allowed to stand at 0 °C for 18 h. The product was collected by filtration under argon and vacuum dried for 18 h at 23 °C (1 mm). The yield of white, crystalline **1f** was 88.1 g (99%), mp 128–130 °C (lit.[17] mp 129–130 °C).

2-(Acetylamino)-5-methoxybenzoic Acid (2d) and 2-Amino-5-methoxybenzoic Acid (3d). Carbonylation of 1.00 g of 1-(acetylamino)-2-bromo-4-methoxybenzene[18] with 0.01 g each of $Pd(PPh_3)_2(Cl)_2$ and PPh_3 gave after hydrolysis as below 0.91 g (46%) of the amino acid **3d**, mp 145–148 °C (lit.[13] mp 148–150.5 °C). Trituration of a similar carbonylation mixture with 3 mL of 10% HCl gave a 0.61-g (77%) crude yield of **2d**. This was dissolved in hot ethanol, and water was added until the solution became cloudy. The solution was filtered to remove some red oil which had separated and cooled at −5 °C overnight. Filtration gave 0.235 g (30%) of tan crystals: mp 160–161 °C (lit.[20] mp 165–166 °C); NMR (Me_2SO) δ 2.13 (s, 3, CH_3CO), 3.83 (s, 3, CH_3O).

Anal. Calcd for $C_{10}H_{11}NO_4 \cdot 5C_2H_5OH$: C, 56.89; H, 6.01; N, 6.03. Found: C, 56.73; H, 5.60; N, 6.01.

2-(Acetylamino)-5-(1-methylethyl)benzoic Acid (2f). A 200-mL glass pressure bottle equipped with two valves and a pressure gauge was charged with 8 mg of $Pd(PPh_3)_2(Cl)_2$, 40 mg of triphenylphosphine, and 2.0 g of **1f**. The bottle was then evacuated, refilled with argon three times, and charged further with 2.2 mL of deoxygenated tri-*n*-butylamine and 0.5 mL of deoxygenated water.[9] The apparatus was then pressurized with 3 atm of carbon monoxide, sealed, heated 18 h with stirring at a bath temperature of 120–125 °C, and then allowed to cool. The

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final pressure was 1.1 atm at 23 °C. Hydrochloric acid (2.4 M) was added to the viscous orange-brown reaction mixture in four 2-mL portions with constant agitation. The crude yield of **2f** which separated (95% pure by NMR) was 1.63 g (94%). Recrystallization from ethanol–water gave 1.35 g (78%) of a light yellow solid: mp 167–170.5 °C; NMR ($CDCl_3$–Me_2SO) δ 1.22 (d, 6, $CH(CH_3)_2$, 2.21 (s, 3, $NHCH_3$), 2.88 (m, 1, $CH(CH_3)_2$), 7.34, 7.89, 8.51 (3 d, 3, Ar H), 9.62 (br, 1, NH), 11.13 (br, 1, CO_2H); IR ($CDCl_3$) 3340 (NH), 2630 (associated OH of CO_2H), 1690 (CO of CO_2H), 1670, 1520 (secondary amide) cm^{-1}.

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.29; H, 6.93; N, 6.39.

2-Amino-5-(1-methylethyl)benzoic Acid (3f). A 300-mL glass autoclave liner was charged with 0.37 g of $Pd(PPh_3)_2(Cl)_2$, 1.8 g (0.0069 mol) of triphenylphosphine and 88.8 g (0.347 mol) of **1f** and then deoxygenated by evacuation/argon refill cycles. The liner was then further charged with 97.7 mL (0.41 mol) of tri-*n*-butylamine and 22.2 mL of water. Carbonylation of this mixture was carried out in a rocking autoclave under ca. 3 atm of CO pressure for 22 h at 115–120 °C. After the autoclave was cooled and vented, the reaction mixture was a viscous oil which was washed from the liner with a total of 900 mL of 10% aqueous NaOH, followed by 95% ethanol (3 × 10 mL). The combined washes are heated 18 h at ca. 95 °C with stirring under argon. The resulting two-phase system was allowed to cool and was then washed with dichloromethane (3 × 100 mL). The combined washings were extracted with 100 mL of 10% NaOH, and the pH of the combined aqueous layers was brought to 3.0–3.5 by addition of aqueous HCl. The acidified aqueous layer was extracted with ethyl acetate (3 × 200 mL), and the extract was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford 53.4 g of crude, crystalline **3f**. Recrystallization from dichloromethane–hexane gave 45.2 g (72%) of **3f**, mp 130–132 °C (lit.[19] mp 130–131 °C). Evaporation of the mother liquors and crystallization of the residue from dichloromethane–hexane gave an additional 7.0 g of **3f**, mp 125–128 °C. According to NMR analysis, the purity of the first crop was 97% and that of the second crop was 95%.

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Registry No. 1a, 614-76-6; **1b**, 79069-35-5; **1c**, 79069-36-6; **1d**, 79069-37-7; **1e**, 79083-83-3; **1f**, 68748-07-2; **2a**, 89-52-1; **2d**, 38985-80-7; **2f**, 79069-38-8; **3b**, 18331-74-3; **3c**, 79069-39-9; **3d**, 6705-03-9; **3e**, 79069-40-2; **3f**, 68701-22-4; 1-bromo-2-methoxybenzene, 578-57-4; 1-bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; 2-hydroxybenzoic acid, 69-72-7; 1-naphthalenecarboxylic acid, 86-55-5; 2-naphthalenecarboxylic acid, 93-09-4; *N*-[4-(1-methylpropy)-phenyl]acetamide, 20331-25-3; *N*-[4-(2-methylpropyl)phenyl]acetamide, 40784-94-9; 2,4-bis(1-methylethyl)aniline, 79069-41-3; 2-bromo-4,6-bis(1-methylethyl)aniline, 79069-42-4; 4-(1-methylethyl)-aniline, 99-88-7; 1-(acetylamino)-4-(1-methylethyl)benzene, 5702-74-9.

Dehydrogenation of Amines. An Approach to Imines and Aldehydes

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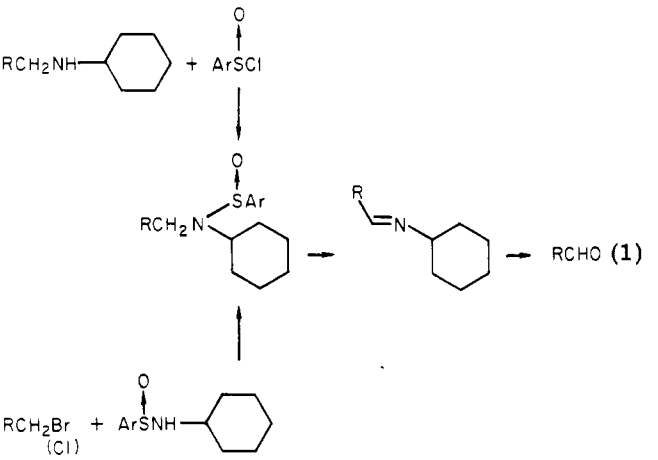
Whereas the sulfenylation–dehydrosulfenylation method has proved useful for the formation of carbon–carbon double bonds,[1] the use of such a method for the introduction of unsaturation to a heteroatom has been almost unexplored. Among the most important is the formation of imines, in part because of their intrinsic importance (such as in cycloadditions to β-lactams) and in part because of their hydrolysis to carbonyl compounds. Contrary to the thiosulfinates[2a] and the sulfinimines[2b] which have relatively labile S–X bonds, the sulfinimide bond is quite strong. While sulfinamides normally are thought to be very stable, their tendency to have a decomposition point rather than a melting point was promising. We report that such a dehydrogenation proceeds well and serves as a convenient method to convert benzylic and allylic halides to imines and aldehydes.[3]

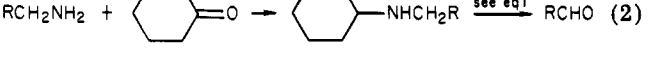
Two approaches to the sulfinamides were employed (eq 1 and Tables I and II). The direct sulfinylation of an



amine proceeded in high yield in ether containing triethylamine. Alternatively, allyl or benzyl bromides (or chlorides) smoothly alkylate *N*-cyclohexylbenzenesulfinamide. While use of sodium hydride as base and DMF as solvent is satisfactory, phase-transfer conditions are preferred. Attempts to use *N*-cyclohexyl-4-nitrobenzenesulfinamide in direct alkylations failed.

Thermolysis of the sulfinamide required use of refluxing xylene. As summarized in Table III, yields were good to excellent. The imine could be isolated by distillation. Chromatographic purification normally effected hydrolysis to the aldehyde. While virtually all of the examples utilized Ar = Ph, a rate enhancement is expected[4] and observed by employing *p*-nitrophenyl.

The regioselectivity of the elimination restricts the method to those cases which contain at least one group which facilitates the elimination. For the present study, the presence of benzylic and allylic activation served such a purpose. The choice of the cyclohexyl substituent was based on (1) the ready availability of cyclohexylamine and cyclohexanone and (2) the minimization of steric hindrance at nitrogen while maximizing the regioselectivity of the elimination away from this substituent. For conversion of a primary amine to an aldehyde, reductive amination (eq 2) produces the requisite cyclohexylamine for dehydrogenation according to eq 1.



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