

Regioselective Carboxylation of Phenols with Carbon Dioxide

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A few novel methods were developed for the regioselective preparation of *p*-hydroxybenzoic acid (*p*HBA) and its amino derivative by means of the Kolbe–Schmitt reaction. Thus, the carboxylation of tetraalkylammonium phenoxide at 125 °C under the CO_2 pressure of 5.0 MPa in the presence of K_2CO_3 gave *p*HBA in a maximum yield of 56% with the regioselectivity of 97–100%. The carboxylation of potassium phenoxide (PhOK) at 230 °C under the CO_2 pressure of 0.5 MPa also gave *p*HBA regioselectively in a 39% yield, together with unaltered phenol (61%). Under such conditions, the potassium salt of salicylic acid (SA) once formed was transformed into *p*HBA. Heat treatment of the dipotassium salt of ^{13}C labeled SA indicated that the transformation occurs via two pathways, i.e., the intramolecular rearrangement of the salicylate (66%) and the decarboxylation of the salicylate followed by the recarboxylation of the resulting PhOK (34%). Furthermore, the carboxylation of cesium *m*-aminophenoxide and 5-amino-1-naphthoxide with CO_2 gave regioselectively 4-hydroxyanthranilic and 8-amino-4-hydroxy-1-naphthoic acids, respectively, in good yields. This is a simple one-pot reaction giving these industrially useful acids with good yields.

The most convenient and popular method for the preparation of aromatic hydroxycarboxylic acids is the carboxylation of alkali metal phenoxides (PhOM) with carbon dioxide (CO_2). The reaction is known as the Kolbe–Schmitt reaction and has been used for over a century.[1] It has been thought for a long time[1] that the reaction proceeds via a complex ($PhOM \cdot CO_2$) composed of PhOM and CO_2. However, recent mechanistic studies[2] have revealed that the reaction proceeds by a direct attack of CO_2 on the benzene ring. The attack occurs on electron-rich *ortho* and *para* positions to give salicylic acid (SA) and *p*-hydroxybenzoic acid (*p*HBA). It is favorable for the industrial production that the attack occurs reigoselectively on the *para* position, since *p*HBA and 6-hydroxy-2-naphthoic acid (2H6NA) prepared from phenol and 2-naphthol, respectively, are key compounds for totally aromatic liquid-crystal polymers. We recently found[3] that cesium phenoxide and 2-naphthoxide give *p*HBA and 2H6NA, respectively, in much higher yields than the widely used methods with sodium or potassium phenoxide and 2-naphthoxide. The prominently selective carboxylation is ascribed to the large ionic radius (0.169 nm[4a]) of cesium, which interferes with the direct attack of CO_2 at the *ortho* positions of the phenoxide and naphthoxide. Sodium and potassium are too small in ionic radii (0.095 and 0.133 nm, respectively[4a]) to interfere effectively with the CO_2 attack at the *ortho* positions.

The present paper describes some experiments directed toward other methods for the regioselective preparation of *p*HBA by the Kolbe–Schmitt reaction. First, we describe the carboxylation of tetraalkylammonium phenoxides ($PhONR_4$), in place of PhOM, by CO_2. Tetraalkylammonium ions (R_4N^+) have larger ionic radii (0.347, 0.400, 0.452, and 0.494 nm for Me_4N^+, Et_4N^+, Pr_4N^+, and Bu_4N^+, respectively[4b]) than alkali metal ions and will effectively interfere with the attack of CO_2 at the *ortho* positions of $PhONR_4$ to give selectively *p*HBA. Second, we describe the carboxylation of PhOK at high temperature and low CO_2 pressure, at which mono- (SAK_1) and dipotassium salicylates (SAK_2) are transformed into potassium salts of *p*HBA.[5,6] The mechanism of the transformation is also discussed on the basis of experiments with ^{13}C-labeled SAK_2. Finally, we describe the regioselective carboxylation of cesium *m*-aminophenoxide and 5-amino-1-naphthoxide with CO_2 to give industrially useful 4-hydroxyanthranilic acid and 8-amino-4-hydroxy-1-naphthoic acid, respectively.

Experimental

Reagents. Phenol, *m*-aminophenol, and alkali metal hydroxides (NaOH, KOH, and $CsOH \cdot H_2O$) were purchased from Kanto Chemical Co. 5-Amino-1-naphthol, carbonates (Na_2CO_3 and K_2CO_3), and sulfate (K_2SO_4) were supplied by Wako Pure Chemical Industries. Tetramethyl- (Me_4NOH), tetraethyl- (Et_4NOH), tetrapropyl- (Pr_4NOH), and tetrabutylammonium hydroxides (Bu_4NOH) were purchased from Aldrich Chemical Co. These chemicals were of guaranteed grade and were used without further purification. CO_2 of purity more than 99.9% and nitrogen were supplied by Sanin Sanso Co. ^{13}C-enriched CO_2 (more than 99%) was supplied by ISOTEC INC (Miamisburg, Ohio, USA).

Preparation of $PhONR_4$. Me_4NOH (0.8 mL of 25 wt % aqueous solution, 2.3 mmol) and phenol (0.2 g, 2.1 mmol) were added to 50 mL of water and stirred for 2–3 min. When necessary, an additive (K_2CO_3, Na_2CO_3, or K_2SO_4) was mixed together. The solution was concentrated on a rotary evaporator at 45 °C. The concentrated solution was lyophilized in a flask at <10 Pa for 30–40 h

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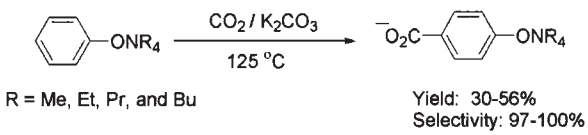
to give tetramethylammonium phenoxide ($PhONMe_4$). $PhONEt_4$, $PhONPr_4$, and $PhONBu_4$ were prepared similarly by mixing phenol (0.2 g, 2.1 mmol) with Et_4NOH (1.0 mL of 35 wt % aqueous solution, 2.3 mmol), Pr_4NOH (2.1 mL of 20 wt % aqueous solution, 2.3 mmol), and Bu_4NOH (1.5 mL of 40 wt % aqueous solution, 2.3 mmol), respectively.

Preparation of PhOM. Phenol (5.00 g, 53.2 mmol) was dissolved in a 100 mL of aqueous solution containing 10% excess alkali metal hydroxides. Water was removed on a rotary evaporator at 80 °C, followed by vacuum drying at 180 °C for 3 h. The prepared phenoxides were ground to fine powders in a dry box under dry nitrogen stream.

General Reactions and Analyses. The prepared $PhONR_4$ or PhOM was placed in an autoclave (200 mL) and CO_2 of a requisite pressure was introduced after flushing with nitrogen. The autoclave was heated quickly to the reaction temperature and maintained there for a requisite reaction time. The reaction mixture in the autoclave was then cooled in a water bath and next dissolved in a small amount of aqueous methanol. The solution was acidified (pH 3–4) with the addition of dilute HCl and analyzed by high-performance liquid chromatography (HPLC) with a column (ODS column 150 × 4.6ϕ mm) on a Shimadzu LC-10 AD chromatograph. ^{1}H NMR spectra were taken in $CDCl_3$ using tetramethylsilane as an internal standard on a JEOL JNM-A400 (400 MHz) spectrometer. Mass spectra were obtained at 70 eV on a Hitachi M-80B spectrometer. All the products were known and were identified by comparing the retention times in HPLC, ^{1}H NMR spectra, and mass spectra with those of the authentic samples.

Results and Discussion

Carboxylation of $PhONR_4$. $PhONR_4$ was subjected to carboxylation under conditions employed in the usual Kolbe–Schmitt reaction. The results are summarized in Table 1. Reaction temperature (125 °C) was somewhat lower than usual (150 °C), since it seemed that $PhONR_4$ was labile and decomposed to give brownish products at 150 °C. Interestingly, the regioselectivity of the carboxylation for *p*HBA was very high, i.e., 96% for $PhONMe_4$ and $PhONEt_4$, and virtually 100% for $PhONPr_4$ and $PhONBu_4$. It is evident that these cations are large enough in size to interfere with the attack of CO_2 on the *ortho* positions of the phenoxide. However, the yields of *p*HBA were low (7–27%), and significant amounts of unaltered phenol were recovered (72–93%). We could not increase the yield of *p*HBA by changing reaction time, temperature, or the mole ratio of the hydroxide to phenol. The only effective method we found was the addition of K_2CO_3 to the reactant. Thus, the carboxylation of $PhONMe_4$ (2.12 mmol) in the presence of K_2CO_3 (1 g, 7.22 mmol) gave *p*HBA in a 56% yield, together with a small amount of alkyl esters of *p*HBA, and the recovery of unaltered phenol decreased to 37%. The regioselectivity for *p*HBA was virtually unchanged (97%). The improving effect of K_2CO_3 was also found in the other $PhONR_4$, though the yields (30–35%) of *p*HBA were significantly less than that in the case of $PhONMe_4$ (Scheme 1). The addition of K_2SO_4, in place of K_2CO_3, to the reactant showed no improving effect, whereas Na_2CO_3 showed an improving effect similar to that of K_2CO_3. It is not clear why K_2CO_3 shows such an improving effect. We can rule out the possibility that K_2CO_3 contributed to increasing the surface area of the reactant in contact with CO_2, since K_2SO_4 showed no such effect. A possible explanation is as follows: The reactant phenol is monobasic acid, whereas the product *p*HBA is dibasic acid. Since the carboxyl group is stronger in acidity than phenol, the carboxyl group of *p*HBA formed will react with neighboring $PhONR_4$ to give the carboxylate ion and inactive phenol. If K_2CO_3 is present in the neighborhood of *p*HBA, the carboxyl group is neutralized by K_2CO_3, and the phenoxide is not consumed for the neutralization of the carboxyl group. There was a fear that a cation-exchange reaction occurs between $PhONR_4$ and K_2CO_3 to form PhOK, of which the regioselectivity for *p*HBA is considerably lower than $PhONR_4$. However, the regioselectivity was unchanged by the addition of K_2CO_3, indicating that the effect of the cation-exchange reaction is mi-



Scheme 1. Regioselective preparation of *p*HBA by the Kolbe–Schmitt reaction of $PhONR_4$.

Table 1. Products in the Carboxylation of $PhONR_4$ (2.1 mol)[a] with CO_2 (5.0 MPa) in a 200 mL Autoclave

Entry	R	Additive	Reaction condition		Recov. phenol	Yield[b] /%				Selectivity for
			Temp.	Time						
		mmol	/°C	/h	/%	SA	*p*HBA	4HIPA	Ester[c]	*p*HBA[d]
1	Me	None	125	2	71.9	1.0	26.5	0.5	0	96
2	Me	K_2CO_3 (7.22)	125	2	37 ± 5	2 ± 0	56 ± 4	3 ± 1	1.4 ± 0.2	97 ± 1
3	Me	K_2SO_4 (7.22)	125	2	90.6	0.6	8.6	0	0	93
4	Et	None	125	5	85 ± 2	0.5 ± 0.1	14 ± 2	trace	0	96 ± 1
5	Et	None	150	2	84.6	3.9	11.3	trace	0	74
6	Et	K_2CO_3 (7.22)	125	2	64 ± 1	0.5 ± 0	30 ± 1	trace	1.0 ± 0.1	99 ± 1
7	Pr	None	125	2	92.8	0	7.1	0	0	100
8	Pr	K_2CO_3 (7.22)	125	2	67 ± 1	trace	30 ± 1	0	3.1 ± 0.9	>99
9	Bu	None	125	5	89 ± 3	trace	11 ± 3	0	trace	>99
10	Bu	K_2CO_3 (7.22)	125	5	56 ± 1	0	35 ± 1	0	10 ± 1	100

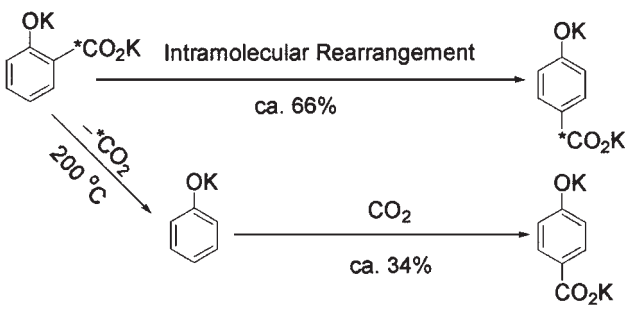
a) $PhONR_4$ was prepared under conditions of $[R_4NOH]/[PhOH] = 1.1–1.5$. b) The mean and standard error are shown for duplicated or triplicated runs. c) The corresponding alkyl *para*-hydroxybenzoates. d) The selectivity was calculated based on the yields of *p*HBA and the corresponding ester, but 4HIPA was not included.

Table 2. Products in the Reactions of PhOK (3.78 mmol), SAK_1 (2.84 mmol), SAK_2 (2.33 mmol), $pHBAK_1$ (2.84 mmol), and $pHBAK_2$ (2.33 mmol) under High (5.0 MPa) or Low (0.5 MPa) CO_2 Pressure for 1 h in a 200 mL Autoclave

Entry	Reactant	Reaction condition		Yield /%			
		CO_2 /MPa	Temp. /°C	phenol	SA	*p*HBA	4HIPA
1	PhOK	0.5	230	61.1	0.0	38.8	trace
2	PhOK	5.0	230	17.0	54.5	2.1	26.0
3	SAK_1	0.5	200	34.2	24.6	40.6	0.8
4	SAK_2	0.5	200	55.0	6.9	34.7	1.0
5	SAK_1	5.0	200	17.4	74.2	trace	8.6
6	SAK_2	5.0	200	1.3	62.1	22.8	13.9
7	$pHBAK_1$	0.5	200	35.2	2.0	60.9	1.0
8	$pHBAK_2$	0.5	200	4.0	0.0	96.0	trace
9	$pHBAK_1$	5.0	200	45.3	4.7	48.5	1.7
10	$pHBAK_2$	5.0	200	1.1	1.9	95.6	1.3

nor, if any. The R_4N^+ and PhO^- ions have large polarizability, and belong to soft acid and base classes, respectively.[7] On the other hand, K^+ and CO_3^{2-} belong to hard acid and base classes, respectively. Thus, the soft PhO^- ion prefers to associate with the soft R_4N^+ ion, rather than with the hard K^+ ion.[7]

Carboxylation of PhOK at High Temperature and Low Pressure. It is known[5,6] that mono- (SAK_1) and dipotassium salicylates (SAK_2) are rapidly converted to the salts of *p*HBA at high temperature above 200 °C and low pressure. Thus, it is anticipated that the carboxylation of PhOK at high temperature and low CO_2 pressure will give regioselectively *p*HBA, since the salicylate once formed is converted to *p*HBA during reaction. In fact, the carboxylation of PhOK at 230 °C and CO_2 pressure of 0.5 MPa gave exclusively *p*HBA in a yield of 34–39% (Table 2), though the recovery of unaltered phenol was significantly high (61–65%). Only minor amounts of SA (less than 0.7%) and 4-hydroxyisophthalic acid (4HIPA, less than 0.1%) were found in the reaction mixture. This result was in sharp contrast to the carboxylation at higher CO_2 pressure of 5.0 MPa: The recovery of phenol was only 17%, and SA and 4HIPA were the main products (55 and 26%, respectively). The yield of *p*HBA was only 2%. It is evident that the salicylate once formed by the direct attack of CO_2 on the *ortho* positions of the phenoxide is transformed into the potassium salt of *p*HBA at low CO_2 pressure of 0.5 MPa. The activation volume of the salicylate for transformation into *p*HBA may be so large that the reaction is unlikely to occur at high CO_2 pressure. In order to confirm this assumption, SAK_1 and SAK_2 were treated at 200 °C for 1 h under the CO_2 pressures of 0.5 and 5.0 MPa (Table 2). The recovery of unaltered SA was 25% for SAK_1 and only 7% for SAK_2 under the CO_2 pressure of 0.5 MPa, whereas the values were 74% for SAK_1 and 62% for SAK_2 under the CO_2 pressure of 5.0 MPa, indicating that the salicylates are reactive at low CO_2 pressure and relatively stable at high CO_2 pressure. SAK_1 and SAK_2 gave *p*HBA in 41% and 35% yields, respectively, together with significant amounts of phenol (28–34%) formed by decarboxylation, after the treatment under the CO_2 pressure of 0.5 MPa. On the other hand, the treatment at the high CO_2 pressure of 5.0 MPa gave only a trace amount of *p*HBA for SAK_1 and a significant amount (23%) of *p*HBA for SAK_2, together with 4HIPA (9–14%). These data show that low CO_2 pressure is advantageous for the regioselective preparation of *p*HBA. Table 2 also contains experimental data in the case of *p*HBA. The mono- and dipotassium salts of *p*HBA were treated under the same conditions as the salicylates. The dipotassium salt of *p*HBA was stable, and the recovery of *p*HBA after treatment was 96%, irrespective of applied CO_2 pressure. The monopotassium salt was less stable, and the recovery decreased to 49–61%. The main product was phenol (35–45%), and small amounts of SA and 4HIPA were involved. The results indicate that the potassium salts of *p*HBA are thermodynamically more stable than those of SA. In order to clarify the pathways in the transformation of the salicylate into the salt of *p*HBA, we prepared SA (SA*) labeled at the carboxyl group with ^{13}C,[2g] and the dipotassium salt of SA* was subjected to heat treatment under the same conditions as described above. The reaction products were esterified to give methyl *p*-hydroxybenzoate (Me*p*HBA) and analyzed by GC/MS as previously reported.[2g] The relative peak intensities of *m*/*z* 152 and *m*/*z* 153 were 100 and ca. 203, respectively, for Me*p*HBA produced by heat treatment under the CO_2 pressure of 0.5 MPa. Virtually the same result was obtained for Me*p*HBA given by treatment under the CO_2 pressure of 5.0 MPa. Considering the natural abundance of ^{13}C (1.1% for each C), we evaluated that ca. 66% of *p*HBA is transformed by the intramolecular rearrangement from the salicylate.[8] The rest (34%) of *p*HBA will be produced via the decarboxylation of the salicylate, followed by recarboxylation at the *para* position of the phenoxide (Scheme 2).

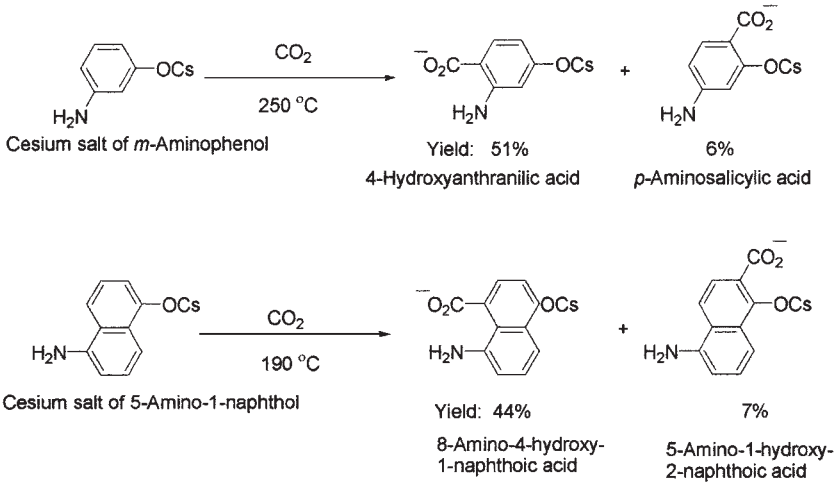


Scheme 2. Two pathways from dipotassium salt of SA to that of *p*HBA.

Table 3. Products in the Carboxylation of Alkali Metal Salts of Aminophenols with CO_2 (5.0 MPa) in a 100 mL Autoclave

Entry	Phenols	Alkali metal	Reaction condition			Yield /%	
			CO_2 /MPa	Temp. /°C	Time /h	*o*-COOH[a)]	*p*-COOH[b)]
1	*m*-Aminophenol	Na	5	200	1	80.0	0
		K	5	200	1	80.0	0
		Cs	5	250	1	5.9	50.6
2	5-Amino-1-naphthol	Na	5	160	3	53.5	0
		K	5	230	5	72.1	0
		Cs	5	190	10	7.2	43.9

a) *ortho*-Carboxylated products, i.e., *p*-aminosalicylic acid for *m*-aminophenol and 5-amino-1-hydroxy-2-naphthoic acid for 5-amino-1-naphthol. b) *para*-Carboxylated products, i.e., 4-hydroxyanthranilic acid for *m*-aminophenol and 8-amino-4-hydroxy-1-naphthoic acid for 5-amino-1-naphthol.



Scheme 3. Regioselective carboxylations of cesium salts of aminophenols.

Carboxylations of Cesium Salts of Aminophenols. We recently found[3] that cesium phenoxide and 2-naphthoxide give *p*HBA and 2H6NA, respectively, in much higher yields than the widely used methods with sodium or potassium phenoxide and 2-naphthoxide. The selective carboxylation is ascribed to the large ionic radius of cesium, which interferes with the direct attack of CO_2 at the *ortho* positions of the phenoxide and naphthoxide. In the present work, we extended the method to the regioselective preparation of industrially useful 4-hydroxyanthranilic and 8-amino-4-hydroxy-1-naphthoic acids from *m*-aminophenol and 5-amino-1-naphthol, respectively. According to reports,[9] *m*-aminophenol gives only *p*-aminosalicylic acid by the ordinary Kolbe–Schmitt reaction with sodium or potassium salts, but not 4-hydroxyanthranilic acid at all. Thus, we investigated an effect of alkali metal ion on product composition after the carboxylation of *m*-aminophenoxide (Table 3). The carboxylation of sodium or potassium salt of *m*-aminophenol under the CO_2 pressure of 5.0 MPa gave only *p*-aminosalicylic acid in a 80% yield. In sharp contrast, the cesium salt gave selectively 4-hydroxyanthranilic acid in a 51% yield, together with a small amount (6%) of *p*-aminosalicylic acid (Scheme 3). This is the simplest one-pot reaction giving the best yield among a number of synthetic methods[10] for 4-hydroxyanthranilic acid. We also examined an effect of alkali metal ion on the product composition after the carboxylation of 5-amino-1-naphtoxide (Table 3). Upon carboxylating the cesium salt, we obtained 8-amino-4-hydroxy-1-naphthoic acid in a good yield (44%), together with 5-amino-1-hydroxy-2-naphthoic acid as a minor product (7%). On the other hand, the sodium and potassium salts gave only 5-amino-1-hydroxy-2-naphthoic acid (54 and 72% yields, respectively). The markedly regioselective *para*-carboxylation of the cesium aminophenoxides will be attributed to the large ionic radius of the cesium ion, which interferes with the direct attack of CO_2 at the *ortho* positions of the aminophenoxides.

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8 In this calculation, we assumed that the incorporation of $^{13}CO_2$ into *p*HBA via the decarboxylation–recarboxylation pathway was negligible, since the amount of $^{13}CO_2$ released from the dipotassium salt of SA* was far less than that of added CO_2. Based on the natural abundance of ^{13}C, we estimated the relative amounts of labeled and unlabeled Me*p*HBA from the GC/MS data as follows: The unlabeled Me*p*HBA gives the peak of m/z 153 with the relative height of ca. 9 ($= 100 \times 0.088$). Then, the relative height of m/z 153 due to the labeled Me*p*HBA is 194 ($= 203–9$). The labeled Me*p*HBA also contains ^{13}C due to natural abundance and gives the peak of m/z 154 with the relative height of 15 ($= 194 \times 0.077$). Thus, the total relative peak heights of labeled and unlabeled Me*p*HBA are 209 ($= 194 + 15$) and 109 ($= 100 + 9$), respectively, and the the relative amounts of labeled and unlabeled Me*p*HBA are 66% [$= 100 \times 209/(209 + 109)$] and 34%, respectively.

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