Observations on Bromine Rearrangement during Demethylation of Bromomethoxybenzoic Acids

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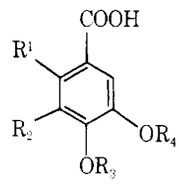
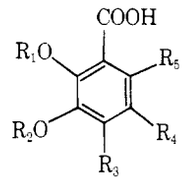
Several aspects of the requirements for concomitant bromine rearrangement during HBr–HOAc demethylation of bromodimethoxybenzoic acids were explored. Formation of 3-bromo-4,5-dihydroxybenzoic acid from 2-bromo-4,5-dihydroxybenzoic acid and isovanillic acid from 2-iodo-4,5-dimethoxybenzoic acid indicated a relationship between halogen loss from its original position and a OH group para to it. This assumption was corroborated when 4-bromo-2,6-dimethoxybenzoic acid resulted in 5-bromoresorcinol. Conversion of 4-bromo-2,3-dimethoxybenzoic acid to 4-bromo-2,3-dihydroxybenzoic acid confirmed the necessity of also locating the halogen to be migrated ortho to the carboxylic acid group. Explanations for these and previous results are proposed.

Perhaps the best studied and most interesting compounds for examining the requisite factors for bromine migration on aromatic compounds (or more aptly, debromination–rebromination) are the bromomethoxybenzoic acids. This series of compounds is well suited to such an investigation since a wide variety of mono- and dimethoxy systems can be devised and synthesized to test several aspects of the mechanism. The various products obtained can be readily analyzed and prepared alternately if needed.

The initial rearrangement observed by Tomita and coworkers[1] when demethylation of 2-bromo-4,5-dimethoxybenzoic acid (**1**) by HBr–HOAc led to 3-bromo-4,5-dihydroxybenzoic acid (**2**) prompted their exploration of several more discernible requirements. For example, they[2-4] found that 2-bromo-3,4-dimethoxybenzoic acid also yields 3-bromo-4,5-dihydroxybenzoic acid (**2**) and 2-bromo-5-methoxybenzoic acid gives 4-bromo-3-hydroxybenzoic acid while 2-bromo-4-methoxybenzoic acid only produces 3-bromophenol. Further experiments indicated that replacement of the carboxylic acid group with an acetyl, aldehyde, or methyl moiety or substitution of chlorine for bromine on the ring caused only ether cleavage but no halogen migration to occur. They also observed that use of 48% HBr as the demethylating reagent formed some rearranged product as well as 3,4-dihydroxybenzoic acid while HCl–HOAc, aqueous HCl, HI, or $AlCl_3$ brought about only demethylation.



1, R_1 = Br; R_2 = H; R_3 = R_4 = Me
2, R_1 = R_3 = R_4 = H; R_2 = Br
6, R_1 = Br; R_2 = R_3 = R_4 = H
7, R_1 = I; R_2 = H; R_3 = R_4 = Me
12, R_1 = R_2 = R_4 = H; R_3 = Me



3, R_1 = R_2 = Me; R_3 = R_4 = R_5 = H
4, R_1 = R_2 = Me; R_3 = R_4 = H; R_5 = Br
5, R_1 = R_2 = R_3 = R_5 = H; R_4 = Br
8, R_1 = R_2 = Me; R_3 = Br; R_4 = R_5 = H
9, R_2 = Me; R_3 = NO_2; R_1 = R_4 = R_5 = H
10, R_1 = R_2 = Me; R_3 = NO_2; R_4 = R_5 = H
11, R_1 = R_2 = Me; R_3 = R_5 = H; R_4 = Br
13, R_1 = R_2 = R_4 = R_5 = H; R_3 = Br
14, R_1 = R_2 = R_3 = R_4 = H; R_5 = Br

Subsequent work by Pettit and Piatak[5] expanded this rearrangement to the *o*-veratric acid (**3**) series by converting 6-bromo-2,3-dimethoxybenzoic acid (**4**) to 5-bromo-2,3-dihydroxybenzoic acid (**5**) and added the nitro group as a potential alternative to the acid moiety by reporting the formation of 3,4-dihydroxynitrobenzene along with 2-bromo-4,5-dihydroxynitrobenzene during reaction of 2-bromo-4,5-dimethoxynitrobenzene with HBr–HOAc.

Results and Discussion

The position and relationships of ring substituents on the starting compounds and their products from the previous work[1-5] implies that the reaction sequence involves (a) demethylation of the methoxyl groups; (b) loss of bromine from the ring as the critical key step; and (c) rebromination of the resultant phenolic acid at a more favorable location. Loss of the bromine atom in the second step appears to occur when it occupies a position which is not favored by simple bromination of the corresponding phenolic acid and is situated either ortho or para to a potential hydroxy group and ortho to the carboxylic acid moiety. The latter criteria have, however, not been rigidly tested since only one example[4] in which the original methoxyl was meta to the bromine was used, and only examples where the halogen atom is ortho to the acid group have been employed. Therefore, we undertook the HBr–HOAc reaction of some model compounds to query the validity of the reaction sequence and provide further information about the character and relationships of the functional groups.

In order to test the first step of the sequence bromohydroxy acid **6** was chosen as a model, since migration of the bromine should occur with this compound even if methoxyl cleavage proceeds initially. Further examination of this part of the mechanism included 6-iodo acid **7**. Hopefully, the more reactive iodine atom[6] would allow for less energetic and, consequently, controllable reaction conditions enhancing the possibility of isolating significant intermediates. Use of iodine would also expand the range of halogens capable of undergoing the rearrangement. Two additional acids, 4-bromo-2,6-dimethoxybenzoic acid and 4-bromo-*o*-veratric acid (**8**), were chosen to verify the necessity of orienting the bromine ortho or para to one methoxy group and ortho to the carboxylic acid moiety.

Of the four desired model compounds only **8** was essentially unknown via a synthetic route. The others could be prepared by available literature methods except for iodo acid **7**, which was best made by direct iodination of veratraldehyde using the iodine–silver trifluoroacetate method[7] followed by oxidation of the aldehyde moiety. The 4-bromo acid **8** prepara-

tion started with the nitration of *o*-vanillin acetate using a combination of procedures by Dey and Kutti[8] and Ichikawa et al.[9] The resultant nitro aldehyde was then oxidized and hydrolyzed to nitro acid **9**, which upon prolonged treatment with diazomethane gave the methyl ester of nitro acid **10**. Comparison of an NMR spectrum of the 4-nitro ester with those of methyl 2,3-dimethoxy-5-nitrobenzoate[10] and methyl 2,3-dimethoxy-6-nitrobenzoate[11] revealed the original structural assignments to be correct.

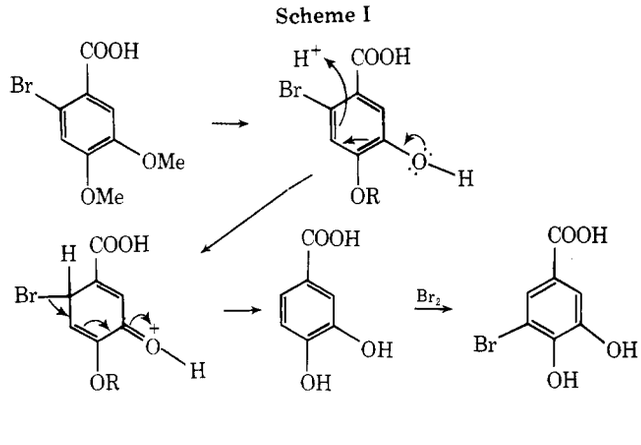
Conversion of the nitro moiety to a bromine and hydrolysis of the resultant bromo ester to the desired 4-bromo acid **8** was carried out without rigid characterization of the two intermediates because they did not crystallize. The desired acid **8** had mp 137–138 °C, quite different from mp 87–89 °C for 6-bromo acid[5] **4** and mp 120 °C for 5-bromo acid[12] **11**. An NMR spectrum of acid **8** had aromatic proton doublets at δ 7.44 and 7.79 with J = 8.5 Hz consistent with the normal coupling constant range of ortho protons. The 6-bromo acid **4** had doublets at δ 6.85 and 7.29 with J = 9.0 Hz indicating the shielding influence of the methoxyl moiety on the adjacent C-4 proton. As might be expected, the aromatic protons for 5-bromo acid **11** appeared at δ 7.25 and 7.85 (J = 2.0 Hz).

Demethylation and/or migration reactions were accomplished in heavy-walled Pyrex tubes. Products were identified by their physical and spectroscopic characteristics and by comparison with specimens synthesized by alternate routes when possible. For example, 5-bromo acid **2** secured from reaction **6** was related to material made by brominating protocatechuic acid.[1] Reaction of 6-iodo acid **7** resulted in isovanillic acid (**12**) identified by mp 250–255 °C (lit.[13] mp 255–257 °C) and an appropriate NMR spectrum. Similarly delineated was 5-bromoresorcinol, the product from reaction of 4-bromo-2,6-dimethoxybenzoic acid, except that it was found to be best characterized as 5-bromo-1,3-dimethoxybenzene.[14]

The structure of 4-bromophenolic acid **13** formed in the HBr–HOAc reaction of 4-bromo acid **8** was also elucidated spectroscopically. Although its melting point (227.5–229 °C) was comparable to that of the potential rearrangement product 5-bromo acid **5** (mp[5] 222–223 °C), an NMR spectrum of **13** had aromatic proton doublets at δ 7.03 and 7.24 (J = 9.0 Hz) which were more appropriate for two ortho protons. An NMR spectrum of **5** had these doublets at δ 7.14 and 7.35 with J = 2.0 Hz while the third isomer, 6-bromo acid[5] **14**, had values of δ 6.73 and 6.86 (J = 7.0 Hz) for its aromatic protons. The identity of **13** was confirmed by comparison with a sample prepared from **8** by $AlCl_3$ demethylation, a method which does not lead to rearrangement.[2,5]

Evaluation of the above and former[1-5] results discloses some unique aspects about the overall reaction and leads us to postulate the mechanism depicted to Scheme I. Initially, cleavage of the methoxy group para (or even ortho) to the halogen will occur. Demethylation of this one in preference to the C-4 methoxyl is favored because the latter will be rendered less basic by the electron-withdrawing effects of the carboxyl.[15] This change will permit the more inductive hydroxyl group to assist protonation of the carbon bearing the halogen. Bromine migration is possible with a para hydroxyl moiety as evidenced by the conversion of 2-bromo acid **6** to 3-bromo acid **2**. alternatively, both methoxy groups could be cleaved before the protonation step but the isolation of isovanillic acid (**12**) from the reaction of iodo acid **7** supports the former interpretation. Rebromination and, hence, halogen migration will result when the formation of protocatechuic acid, which promotes bromination at C-5, is complete.

Scheme I



The decarboxylation of 4-bromo-2,6-dimethoxybenzoic acid during its demethylation coupled with the previous[3] conversion of 2-bromo-4-methoxybenzoic acid to 3-bromophenol tends to also confirm the supposition that the halogen should be ortho or para to at least one oxygen functionality. In both of these examples, one or more methoxy groups were situated meta to the bromine while the carboxylic acid was either ortho or para.

Perhaps the most curious outcome is the isolation of 4-bromophenolic acid **13**, a product of only demethylation, from bromo acid **8**. It appears that bromine loss from the aromatic rings is greatly influenced by its position with respect to the acid group. It can best be explained by a deactivating effect of the carboxyl group upon protonation of the C-4 position bearing the bromine.[15] This effect apparently negates any activating influence by the ortho oxygen moiety. When the carboxylic acid is located ortho to the bulky bromine (Scheme I), however, it is twisted out of plane and loses a large part of its influence permitting the hydroxyl group para to the bromine to assist protonation and, thus, bring about bromine loss.

Experimental Section

The ^1H NMR spectra were recorded with a Varian A-60A instrument. Unless otherwise noted, $CDCl_3$ was used as the solvent with Me_4Si as the internal standard. IR spectra were taken on KBr disks with a Perkin-Elmer 237B instrument. Melting points are uncorrected and were observed with a Fisher-Johns apparatus.

HBr–HOAc Reaction of 2-Bromo-4,5-dihydroxybenzoic Acid (6). The 2-bromo acid[2] (0.5 g) was heated with a 46% HBr–HOAc solution (10 ml) in a sealed tube for 3 h at 130 °C. The solution was evaporated under a stream of nitrogen, and the product was recrystallized from water to yield 3-bromo acid **2** [mp 226–228 °C (lit.[1] mp 222 °C); NMR (Me_2SO) δ 7.44 (d, 1, J = 2.0 Hz), 7.59 (d, 1, J = 2.0 Hz)], identical in all respects with a sample prepared by brominating 3,4-dihydroxybenzoic acid.[1]

2-Iodo-4,5-dimethoxybenzaldehyde. A solution of iodine (29.2 g) in CCl_4 (160 ml) was added to veratraldehyde (19.0 g) and CF_3CO_2Ag (25.0 g) with shaking. The reaction mixture was stirred for 4 h, the yellow AgI collected by filtration, and the filtrate washed with 5% $NaHSO_3$. Removal of the solvent and crystallization of the residue from methanol (500 ml) gave 27.0 g (81.9%) of the 2-iodoaldehyde: mp 145–146 °C; NMR δ 3.88 (s, 3), 3.92 (s, 3), 7.27 (s, 1), 7.34 (s, 1), 10.12 (s, 1).

Anal. Calcd for $C_9H_9IO_3$: C, 37.01; H, 3.11. Found: C, 36.95; H, 3.13.

Rilliet[16] reported mp 128 °C for this compound obtained via diazotization of 2-amino-4,5-dimethoxybenzaldehyde and reaction with KI.

2-Iodo-4,5-dimethoxybenzoic Acid (7). The iodo aldehyde (13.1 g) was oxidized by addition to $KMnO_4$ (37.0 g) in water (200 ml). The mixture was heated at 40 °C with stirring for 1.5 h, then filtered. Acidification of the filtrate and recrystallization of the product from ethanol–water gave 3.29 g (28%): mp 159–160 °C; NMR δ 3.71 (s, 3), 3.75 (s, 3), 7.38 (s, 1), 7.42 (s, 1).

Anal. Calcd for $C_9H_9IO_4$: C, 35.08; H, 2.95. Found: C, 34.52; H, 2.97.

HBr–HOAc Reaction with 2-Iodo-4,5-dimethoxybenzoic Acid (7). A 0.5-g sample of iodo acid **7** was heated at 50 °C with 10 ml of 46% HBr/HOAc overnight. Some decomposition occurred as evidenced by the darkness of the reaction. Removal of the solvent under a stream of nitrogen and recrystallization of the residue from water yielded 0.16

g of isovanillic acid (12), mp 216–220 °C. Recrystallization from water (Norite A) resulted in mp 250–255 °C (lit.[13] mp 255–257 °C); NMR δ 3.89 (s, 3), 6.94 (d, 1, J_{AB} = 9.0 Hz), 7.35 (d, 1, J = 1.7 Hz), 7.41 (1, J_{AB} = 9.0, J_{AM} = 1.7 Hz).

Demethylation of 4-Bromo-2,6-dimethoxybenzoic Acid. A sample of 4-bromo-2,6-dimethoxybenzoic acid[17] (0.5 g) was sealed in a glass tube with 40% HBr in glacial HOAc (5 ml). The tube was heated to 130 °C during 100 min, kept at 130–142 °C for 65 min, and then cooled. The solution was evaporated in vacuo, and the residue was taken up in ether and washed with dilute $NaHCO_3$ and water. The product was treated with diazomethane overnight. Recrystallization of the methylated material from MeOH–petroleum ether gave 0.3 g (75%) of 5-bromo-1,3-dimethoxybenzene: mp 60.5–62.5 °C; ν_{max} 1580, 1215, 1165, 1050 cm^{-1}; NMR δ 3.74 (s, 6), 6.35 (t, 1, J = 2.0 Hz), 6.62 (d, 2, J = 2.0 Hz). A melting point of 66 °C was reported by Dean and Whalley.[14]

4-Nitro-2-hydroxy-3-methoxybenzaldehyde. A procedure combining the methods of Dey and Kutti[8] and Ichikawa et al.[9] gave the best results. Finely powdered *o*-vanillin acetate (30 g) was added to a stirred mixture of fuming HNO_3 (100 ml) and concentrated H_2SO_4 (20 ml) at −15 °C over 1 h. After the reaction mixture had been stirred for 40 min at −5 to −15 °C, it was poured into ice water (ca. 700 g). The resultant oil was recovered with benzene and washed with dilute $NaHCO_3$ and water. Recrystallization of the residue from methanol gave 12 g of material, mp 134–137 °C, which proved to be two compounds by TLC.

All of the nitrated material was therefore hydrolyzed in 2% NaOH (700 ml) by refluxing for 20 min. Storage of the solution overnight at ambient temperature gave an orange precipitate which was collected. Acidification of the filtrate yielded the 4-nitro isomer which was recrystallized from methanol–water (Norite A) to give 22 g (72.2%) of product with mp 92–93.5 °C; ν_{max} 3100, 1670, 1525 cm^{-1}. A melting point of 92–93 °C was reported by both Dey and Kutti[8] and Ichikawa et al.[9]

The orange precipitate from the hydrolysis was suspended in hot water and acidified. The resultant brown material was recrystallized from methanol (Norite A) to yield the 6-nitro isomer as yellow needles: mp 104–107 °C; ν_{max} 3050, 1670, 1500 cm^{-1}. Ichikawa[9] reported mp 104 °C, while Dey and Kutti[8] observed only 72–73 °C.

4-Nitro-2-hydroxy-3-methoxybenzoic Acid (9). Silver nitrate (50 g) was added to the above 4-nitro aldehyde (10 g) suspended in a solution of NaOH (22 g) in water (1 l.) at 70 °C. The mixture was refluxed for 5 h, then filtered hot. Acidification of the filtrate formed a brown precipitate which was recrystallized from methanol–water (Norite A) to yield 6 g (55.5%) of pale yellow flakes, mp 205–206.5 °C. Repeated recrystallization from the same solvent gave an analytical sample of **9** with mp 206.5–208 °C; ν_{max} 3000, 1640, 1510 cm^{-1}; NMR δ 3.74 (s, 3), 7.32 (d, 1, J = 8.7 Hz), 7.72 (d, 1, J = 8.7 Hz).

Anal. Calcd for $C_8H_7NO_6$: C, 45.08; H, 3.31; N, 6.57. Found: C, 44.96, 45.06; H, 2.97, 3.43; N, 6.59, 6.76.

The nitro acid **9** was methylated with diazomethane to methyl 4-nitro-2-hydroxy-3-methoxybenzoate which had mp 112–114 °C (from methanol); ν_{max} 3130, 1680, 1540 cm^{-1}; NMR δ 4.01 (s, 3), 4.05 (s, 3), 7.16 (d, 1, J = 8.0 Hz), 7.67 (d, 1, J = 8.0 Hz).

Anal. Calcd for $C_9H_9NO_6$: C, 47.58; H, 3.99; N, 6.17. Found: C, 47.77; H, 3.98; N, 6.43.

Methyl 4-Nitro-2,3-dimethoxybenzoate. Freshly prepared diazomethane (ca. 6 g) in ether was added to nitro acid **9** (6.0 g) dissolved in ether, and the solution was stored for 3 days at room temperature. Removal of the solvent and crystallization of the residue from methanol resulted in 2.5 g (36.8%) of ester which gave an analytical sample having mp 40–42 °C; ν_{max} 1750, 1555 cm^{-1}; NMR δ 3.94 (s, 3), 3.98 (s, 3), 4.03 (s, 3), 7.55 (s, 2).

Anal. Calcd for $C_{10}H_{11}NO_6$: C, 49.80; H, 4.60; N, 5.81. Found: C, 50.25, 50.16; H, 4.66, 4.33; N, 5.53, 5.57.

Hydrolysis of the ester with 2 N KOH on a steam bath for 2 h and acidification of the red solution gave 4-nitro acid **10:** mp 157–159 °C; ν_{max} 3190, 1735, 1595, 1630, 1470 cm^{-1}. Majima and Okazaki[18] indicated mp 94–95 °C for the 4-nitro acid they obtained by oxidizing 2,3-dimethoxy-4-nitrotoluene.

4-Bromo-2,3-dimethoxyoxbenzoic Acid (8). The 4-nitro ester (1.0 g) was reduced with 10% Pd/C (75 mg) in ethanol (20 ml) under 3 atm hydrogen. The catalyst was removed with Celite, and the filtrate evaporated to give an oil with infrared bands at 3440, 1670, 1580 cm^{-1} and NMR signals at δ 3.83 (s, 6), 3.90 (s, 3), 4.60 (s, 2), 6.48 (d, 1, J = 8.5 Hz), 7.49 (d, 1, J = 8.5 Hz).

The amino ester was taken up in water (20 ml) containing 48% HBr (4.0 ml) and cooled to 5 °C. A solution of $NaNO_2$ (0.37 g) in water (1.5 ml) was introduced, and the mixture was stored at 5 °C for 1 h. A slurry of CuBr prepared from $CuSO_4$ (0.7 g), NaBr (1.8 g), concentrated H_2SO_4 (0.7 g), Cu powder (0.44 g), and water (10 ml) was added, and the diazotization mixture was stirred at ambient temperature overnight. The product was recovered with ether. It failed to crystallize, but had infrared bands at 1700 and 1550 cm^{-1} and NMR signals at δ 3.91 (s, 3), 3.95 (s, 6), 7.34 (s, 2).

The bromo ester was hydrolyzed with 5% NaOH (20 ml) by heating at reflux for 2.5 h. The reaction mixture was filtered, and the filtrate acidified. The bromo acid **8** was recovered with ether and crystallized from methanol to yield 1.06 g (98.2%), which gave an analytical sample after repeated recrystallizations from the same solvent. It had mp 137–188 °C; ν_{max} 2970, 1690, 1585 cm^{-1}; NMR δ 3.93 (s, 3), 4.13 (s, 3), 7.44 (d, 1, J = 8.5 Hz), 7.79 (d, 1, J = 8.5 Hz).

Anal. Calcd for $C_9H_9BrO_4$: C, 41.39; H, 3.47. Found: C, 41.59, 41.76; H, 3.19, 3.51.

4-Bromo-2,3-dihydroxybenzoic Acid (13). A. HBr–HOAc Reaction. A 0.2-g sample of bromo acid **8** was sealed in a tube with 6.0 ml of a 40% solution of HBr gas in glacial HOAc. The tube was heated to 130 °C in 100 min, maintained at 130–140 °C for 65 min, then cooled. The red solution was evaporated in vacuo, water added to the residue, and the mixture evaporated again. Since an NMR spectrum indicated the presence of acetate moieties, the material was treated with 5% NaOH (10 ml) for 1 h on a steam bath. Acidification of the solution, recovery of the acid with ether, and recrystallization of the product from methanol–water gave 0.1 g (55.5%), mp 227.5–229 °C. Repeated recrystallizations from the same solvent produced **13** melting at 226–228 °C; ν_{max} 3545, 2950, 1680 cm^{-1}; NMR (Me_2SO) δ 7.03 (d, 1, J = 9.0 Hz), 7.24 (d, 1, J = 9.0 Hz).

Anal. Calcd for $C_7H_5BrO_4$: C, 36.08; H, 2.16. Found: C, 35.75, 35.84; H, 2.21, 2.13.

DaRe and Cimatoribus[19] reported the isolation of 4-bromo-2,3-dihydroxybenzoic acid, mp 225–227 °C, from a natural source.

B. $AlCl_3$ Reaction. Anhydrous $AlCl_3$ (2.5 g) was added to bromo acid **8** in benzene (16 ml), and the mixture was refluxed for 4 h. Additional $AlCl_3$ (1.5 g) was introduced and refluxing was continued for 2 h. The cooled reaction mixture was decomposed with concentrated HCl (10 ml) and water (7 ml), and the product isolated with ether. Recrystallization of acid **13** from methanol–water yielded 0.8 g (44.4%), mp 224–228 °C, identical with the sample from A by mixture melting point and comparison of infrared and NMR spectra.

Registry No.—2, 61203-46-1; **6,** 61203-47-2; **7,** 61203-48-3; **8,** 61203-49-4; **9,** 61203-50-7; **10,** 61203-51-8; **12,** 645-08-9; **13,** 61203-52-9; 2-iodo-4,5-dimethoxybenzaldehyde, 61203-53-0; iodine, 7553-56-2; veratraldehyde, 120-14-9; 4-bromo-2,6-dimethoxybenzoic acid, 61203-54-1; 5-bromo-1,3-dimethoxybenzene, 20469-65-2; 4-nitro-2-hydroxy-3-methoxybenzaldehyde, 20041-61-6; *o*-vanillin acetate, 7150-01-8; HNO_3, 7697-37-2; 6-nitro-2-hydroxy-3-methoxybenzaldehyde, 2426-86-0; diazomethane, 334-88-3; methyl 4-nitro-2-hydroxy-3-methoxybenzoate, 61203-55-2; methyl 4-nitro-2,3-dimethoxybenzoate, 61203-56-3; methyl 4-amino-2,3-dimethoxybenzoate, 61203-57-4; methyl 4-bromo-2,3-dimethoxybenzoate, 61203-58-5; $AlCl_3$, 7446-70-0.

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