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Rearrangement of *o*-Hydroxy Aldehydes and Ketones to *o*-Hydroxy Anilides by Monochloroamine[1]

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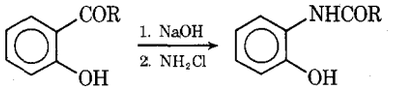
o-Hydroxy aldehydes and ketones are converted in good yield to *o*-hydroxy anilides by reaction with monochloroamine in base. The reaction was carried out with benzene nuclei containing alkyl, methoxyl, chlorine, and nitro substituents, as well as with the naphthalene nucleus. The overall transformation is similar to the Beckmann, Schmidt, Theilacker, and Pearson rearrangements. There appears to be mechanistic similarity to the Dakin oxidation.

The literature contains a number of rearrangement techniques for conversion of aromatic aldehydes and ketones to the corresponding anilides, including those of Beckmann,[3] Schmidt,[4] Theilacker,[5] and Pearson.[6] Each of these is characterized by certain limitations.

We have found a new method for the preparation of *o*-hydroxy anilides involving reaction of monochloroamine with variously substituted *o*-hydroxy aldehydes and ketones. This simple, one-step rearrangement, which takes place under mild conditions, comprises the preferred route for certain anilides. The mechanistic aspects were also investigated.

Results and Discussion

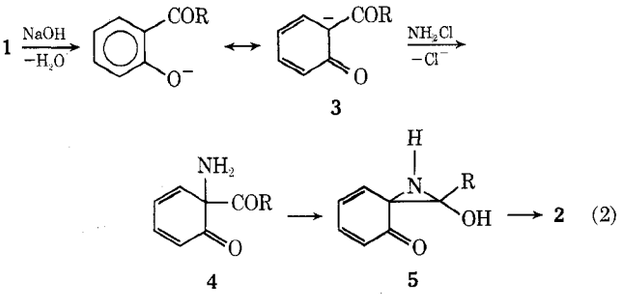
2-Acetamidophenol (**2a**) was obtained in essentially quantitative yield from addition of a caustic solution containing *o*-hydroxyacetophenone (**1a**) to aqueous monochloroamine at about 0°. The infrared spectrum of **2a** corresponded to that of authentic material. 2-Formamidophenol (**2b**), which displayed characteristic infrared absorption bands for the amide moiety, was obtained in similar manner in excellent yield from salicylaldehyde (**1b**). The melting points corresponded to the reported values. The structural assignments are also in agreement with the nmr spectra.



(1)

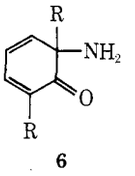
1a, R = CH_3 **2a**, R = CH_3
b, R = H **b**, R = H

The reaction pathway, eq 2, conceivably involves nucleophilic displacement of chloride ion from monochloroamine by the cyclohexadienone (phenoxide) anion (**3**) to produce amino ketone **4**. Intermediate **4** is then converted to aziridine **5**, which undergoes rearrangement to anilide **2**.



(2)

Formation of **4** is analogous to the postulate, involving **6**, advanced by Paquette for conversion of 2,6-disubstituted



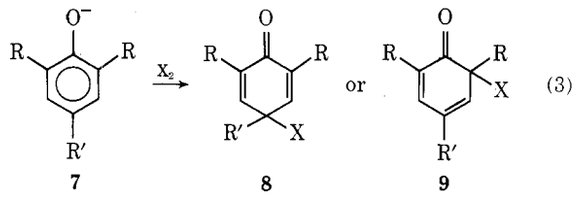
6

phenoxides into dihydroazepinones *via* ring expansion by exposure to monochloroamine.[7] Kornblum and coworkers noted that the extent of C-alkylation of phenoxides increased in hydroxylic solvent.[8]

An aziridine intermediate has also been invoked in the conversion of *N,N*-dichloroamines to α-amino ketones.[9] Monochloroamine has been used[10] for amination of malonic esters, perhaps *via* a route analogous to the transformation of **3** to **4**.

A factor weighing against involvement of dienone **4** is the difficulty of forming this type of species, according to the prior literature. Thus, it is reported[11a] that reaction of **7**

with halogen produces only **8** when R′ is electron donating (alkyl or methoxymethyl), eq 3. However, with an electron-

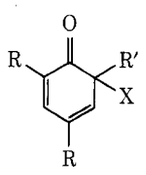


(3)

7 **8** **9**

R = alkyl

withdrawing substituent (NO_2, CN, CHO, halogen) in the para position, the observed product is **9**. In addition, we were unable to find[11b] analogs of **8** (R′ = electron-withdrawing group) when electrophiles other than halogen were used, or compounds of type **10** (R′ = electron-withdrawing

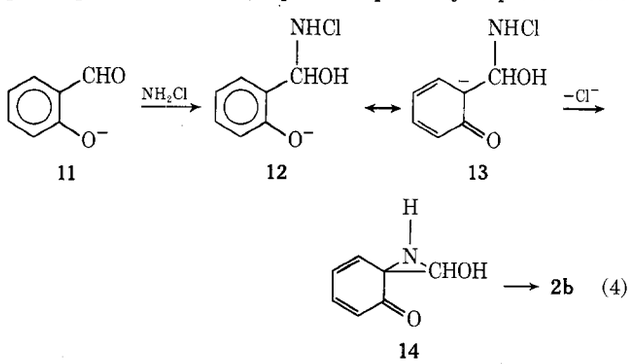


10

R = alkyl

group; X = electrophile). On the other hand, it is conceivable that reaction with NH_2Cl may be kinetically controlled, whereas certain other cases may reflect thermodynamic control.[11c]

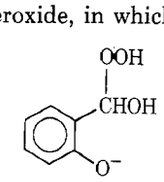
Benzaldehydes are known[12] to react with monochloroamine to produce *N*-chloroimines, presumably through the intermediacy of *N*-chlorocarbinolamines which might participate in our case, eq 4. The pathway depicted bears



(4)

11 **12** **13** **14**

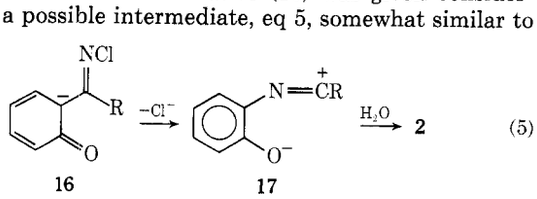
resemblance to that suggested[13] for Dakin oxidation of *o*-hydroxy aldehydes and ketones to dihydroxybenzenes by means of alkaline peroxide, in which **15** may be involved.



15

Our rearrangement, as well as that of Dakin, might well proceed in a concerted manner. A related example[14] entails transformation of *p*-$HOC_6H_4CH_2CH_2Br$ to spiro[2.5]octa-1,4-dien-3-one in the presence of base.

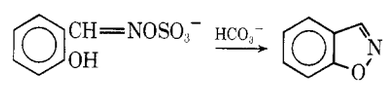
The *N*-chloroimine derivative (**16**) was given consideration as a possible intermediate, eq 5, somewhat similar to



(5)

16 **17**

the Theilacker rearrangement.[5] However, there was no evidence for formation of this type of entity. In addition, acetophenone was recovered almost quantitatively when subjected to the standard procedure. It is significant that the *N*-chloroimine of acetophenone was stable when exposed to the usual conditions. In contrast, hydroxylammonium *O*-sulfonate combined with salicylaldehyde to give **18** which, on exposure to mild base, provided **19**,[15] eq 6.



(6)

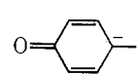
18 **19**

Further evidence in opposition to **16** derives from the generation of *N*-methyl-2-acetamidophenol from methylmonochloroamine and *o*-hydroxyacetophenone in caustic solution. This appears to be the first example of an N,N-disubstituted amide arising from rearrangement of a carbonyl compound or its derivative.

Finally, one can visualize the existence of a nitrene,[16] acting as a precursor for **4**, from α-elimination involving monochloroamine. This approach bears resemblance to the synthesis of cyclohexadienones from substituted phenoxides and dichlorocarbene under Reimer–Tiemann conditions.[17] However, the elimination route appears unlikely since 67% of positive chlorine remained in a caustic solution of monochloroamine after 5 hr at 0°.

When the reaction between monochloroamine and *o*-hydroxyacetophenone was carried out at room temperature, rather than at 0°, 2,2′-dihydroxyacetophenone azine was isolated in addition to rearranged product. Apparently, under these conditions, hydrazine is formed[12] *in situ* from monochloroamine and excess ammonia, and subsequently condenses with the carbonyl-containing substrate.

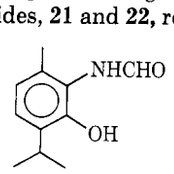
Several experiments were conducted in order to determine the effect of the position of the hydroxyl group in the aromatic nucleus. In contrast to the situation with the corresponding ortho isomers, 4-formamidophenol and 4-acetamidophenol were obtained in only about 10% yield from *p*-hydroxylbenzaldehyde and *p*-hydroxyacetophenone, respectively. The poor results probably reflect the increased stability of the *p*-quinoid (**20**) *vs.* the corresponding *o*-qui-



20

noid structure, or preference for an alternate pathway.[13] The importance of carbanion character associated with the nuclear carbon α to the carbonyl group (as in **3**) is indicated by the failure of *m*-hydroxyacetophenone and *o*-methoxyacetophenone to give rearranged products. Additional support for the crucial role of the *o*-hydroxyl group is provided by the absence of reaction with acetophenone.

The scope of the reaction was explored in relation to the effect of various substituents in the salicylaldehyde nucleus. Methoxyl functioned well when situated adjacent to hydroxyl, providing 2-formamido-6-methoxyphenol in good yield. 3-Nitro- and 5-chlorosalicylaldehyde rearranged smoothly to the corresponding formamidophenols. Salicylaldehydes derived from naturally occurring thymol and carvacrol produced good yields of the corresponding formamides, **21** and **22**, respectively. Nuclear chlorination[12]



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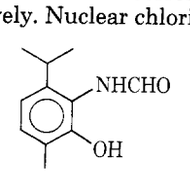
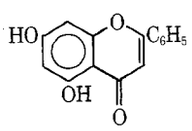


22

accompanied rearrangement with more highly activated aromatics, such as 4,6-dimethoxy-2-hydroxybenzaldehyde and 4,6-dimethyl-2-hydroxyacetophenone. With 2-hydroxy-1-naphthaldehyde, the corresponding amide, 1-formamido-2-naphthol, was provided. This may well be the preferred method for preparation of those products containing the methoxyl, chloro, and nitro groups. The anilides could then serve as precursors for the corresponding amines, as demonstrated in the hydrolysis of **2a** to *o*-aminophenol.

Variations were made in the nature of the substituents attached to the aroyl group in order to obtain further mechanistic and synthetic insight. In addition to **1a** and **1b**, *o*-benzoylphenol was examined, which afforded 2-benzamidophenol in 75% yield. More complex compounds containing the *o*-hydroxybenzoyl unit were explored. 1,8-Dihydroxyanthraquinone was not affected, possibly because of its low solubility in the medium. Chrysin (**23**) was recovered unchanged, whereas naringenin (**24**) yielded uncharacterized, high-melting material which was difficult to



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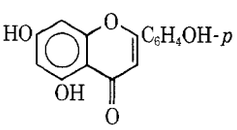

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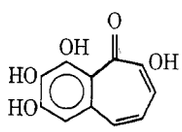

25

purify. More drastic changes were made in the nature of the organic substrate. Tropolone was not altered and purpurogallin (**25**) gave unidentified, high-melting product. Several rationalizations come to mind concerning the failure of rearrangement in these cases: (1) in some instances a more highly strained cyclic amide would ensue, and (2) most of the substrates ontained the *p*-hydroxybenzoyl unit, which appears to affect rearrangement adversely (see above).

In a further study of reaction scope, related unsaturated groups were used in place of the carbonyl moiety. However, no rearrangement was observed with *o*-hydroxybenzonitrile, ethyl salicylate, or *N*-phenylsalicylamide. Concerning the observed specificity, contributing factors may be appropriate resonance stabilization of the carbanion (such as **3**) by the unsaturated substituent, and the fact that aldehydes and ketones are more susceptible to nucleophilic attack; see eq 4.

With few exceptions,[18] catalysts for Beckmann rearrangement of aromatic aldoximes produce little or no formanilides.[3] Thus, rearrangement of salicylaldoxime afforded only salicylamide in 47% yield with BF_3 catalyst.[3]

Mass spectral studies of several of the hydroxy anilide products (**2b**, **22**, and 4-chloro-2-formamidophenol) revealed an intense M − 2 peak. This type of behavior has been previously reported for 1,4-dihydroxybenzenes.[19] In our case, iminoquinoid type moieties are presumably generated in the spectrometer. In addition, a strong M − 18 peak was observed, probably from formation of benzoxazoles.

Experimental Section

Ir spectra were obtained with KBr pellets. Elemental analyses were performed by Baron Consulting Co., Orange, Conn., and Dr. R. E. White. Anhydrous sodium sulfate was used for drying.

Preparation of Monochloroamine.[12] Cold (about 0°) aqueous solutions of 6% ammonia and 6% sodium hypochlorite were mixed in equal (w/w) percentage composition (NH_3:NaOCl = 2.8:1 M). The product molarity was determined by titration with 0.10 *N* sodium thiosulfate.

Preparation of Methylmonochloroamine.[12] A mixture of methylamine hydrochloride (0.06 mol) in 6% sodium hypochlorite (50 ml, 0.05 mol) was stirred for 30 min in an ice bath at *ca.* 0°. The product molarity was determined by titration with 0.10 *N* sodium thiosulfate.

General Procedure for Rearrangement. A solution of the *o*-hydroxy aldehyde or ketone (0.05 mol) in 100 ml of water containing sodium hydroxide (0.05 mol) was slowly added to a vigorously stirred solution of monochloroamine (0.05 mol) at about 0°. After the reaction mixture was agitated for 4 hr at about 0°, it was extracted with ether. The extract was dried, and solvent was removed under vacuum. In general, a negligible amount of residue was found. The cold, aqueous solution was acidified with cold 18% hydrochloric acid. At this stage either the precipitate was collected or the oil was taken up in ether. Removal of solvent from the dried extract afforded rearranged product which gave a light tan solid after crystallization, except for the nitro compound (yellow).

The indicated molar ratios were used in the individual cases, NH_2Cl:substrate: 0.02:0.0004, 1,8-dihydroxyanthraquinone; 0.02:0.01, **24**; 0.02:0.01, **25**; 0.02:0.01, **23**; 0.03:0.02, 2-hydroxy-3-methoxybenzaldehyde; 0.02:0.02, 2,4-dimethoxy-6-hydroxybenzaldehyde; 0.02:0.02, 2-hydroxy-3-nitrobenzaldehyde; 0.03:0.02, tropolone; 0.04:0.02, 1-formyl-2-naphthol; 0.01:0.01, *o*-benzoylphenol; 0.01:0.01, *o*-thymolaldehyde; 0.01:0.01, carvacrolaldehyde; 0.01:0.01, 2-hydroxy-4,6-dimethylacetophenone; 0.01:0.01, 5-chlorosalicylaldehyde.

Since 1,8-dihydroxyanthraquinone was found to be quite insoluble in the caustic medium, the quantity of base was doubled without apparent appreciable increase in solubility.

When the reaction was performed at 24° with **1a**, a precipitate of 2,2′-dihydroxyacetophenone azine was formed which was filtered and crystallized from ethanol: 4.6% yield; mp 197–198° (lit.[20a] mp 198°); ir 1608, 1300, 1249, 1158, 842, and 757 cm^{-1}; nmr ($CDCl_3$) δ 2.56 (s, 6 H), 6.80–7.70 (m, 8 H), and 9.50 (s, 2 H). Elemental analyses (C, H, N) were in accord with the formula $C_{16}H_{16}N_2O_2$. Rearranged product was obtained in 54% yield.

Characterization of Products. Compound **2a** was crystallized from a mixture of ether and petroleum ether (bp 35°): 99% yield; mp 203–205° (lit.[21,22] mp 203–204°); ir 3360, 3030, 1663, 1595, 1539, 1450, and 770 cm^{-1}; nmr (DMSO-d_6) δ 2.1 (s, 3 H), 6.9–7.8 (m, 4 H), 9.3 (s, 1 H), and 9.7 (s, 1 H). Elemental analyses (C, H, N) were in accord with the formula $C_8H_9NO_2$.

Compound **2b** was crystallized from a mixture of ether and petroleum ether: 87% yield; mp 127–128° (lit.[21] mp 129–129.5°); ir 3250, 2980, 1640, 1437, 1357, 870, 838, 756, and 744 cm^{-1}; nmr (DMSO-d_6) δ 6.60–7.15 (m, 4 H), 8.30 (s, 1 H), 9.50 (broad s, 1 H), and 9.83 (s, 1 H).

2-Formamido-6-methoxyphenol was crystallized from a mixture of ether and petroleum ether: 75% yield; mp 123–124°; ir 3260, 3060, 1665, 1470, 1265, 1222, 1068, 903, and 704 cm^{-1}; nmr (DMSO-d_6) δ 3.87 (s, 3 H), 6.60–6.90 (d, 2 H), 7.6–7.9 (m, 1 H), and 9.23 (s, 1 H).

Anal. Calcd for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.56; H, 5.63; N, 8.34.

1-Formamido-2-naphthol was crystallized from a mixture of benzene and cyclohexane: about 24% yield; mp 205–206° (lit.[20b] mp 204°); ir 3205, 1665, 1508, 1318, 980, 772, and 760 cm^{-1}; nmr (DMSO-d_6) δ 6.99–8.00 (m, 6 H), 8.33 (s, 1 H), and 9.13–10.10 (q, 2 H).

2-Formamido-6-nitrophenol was crystallized from a mixture of benzene and cyclohexane: 99% yield; mp 168–169°; ir 3210, 1670, 1605, 1527, 1258, 924, and 748 cm^{-1}; nmr (DMSO-d_6) δ 6.63–7.01 (t, 1 H), 7.55–7.80 (d, 1 H), 8.42 (broad s, 2 H), 9.97 (br, 1 H), 10.66 (br, 1 H).

Anal. Calcd for $C_7H_6N_2O_4$: C, 46.16; H, 3.32; N, 15.38. Found: C, 46.01; H, 3.55; N, 15.36.

2-Benzamidophenol was crystallized from a mixture of ether and petroleum ether: 75% yield; mp 166.5–167.5° (lit.[23] mp 167°); ir 3320, 2970, 1642, 1532, 1445, 750, 705, and 688 cm^{-1}; nmr (DMSO-d_6) δ 6.70–8.20 (m, 9 H), 9.56 (s, 1 H), and 9.76 (s, 1 H).

N-Methyl-2-acetamidophenol was crystallized from a mixture of ether and petroleum ether: 19% yield; mp 152–153°; ir 3210, 1642, 1490, 836, and 765 cm^{-1}; nmr ($CDCl_3$) δ 1.90 (s, 3 H), 3.24 (s, 3 H), 6.70–7.30 (m, 4 H), and 8.95–9.40 (broad s, 1 H).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.04; H, 6.67; N, 8.42.

3-Isopropyl-6-methyl-2-formamidophenol (**22**) was crystallized from a mixture of benzene and petroleum ether: 75% yield; mp 144–146°; ir 3250, 1630, 1600, 807, and 741 cm^{-1}; nmr (acetone-d_6) δ 1.12 (d, 6 H), 2.10 (s, 3 H), 2.95 (s, 1 H), 3.00 (m, 1 H), 6.84 (q, 2 H), 7.88 (s, 1 H), and 8.32 (s, 1 H).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.65; H, 7.98; N, 7.22.

6-Isopropyl-3-methyl-2-formamidophenol (**21**) was crystallized from a mixture of benzene and petroleum ether: 76% yield; mp

135–136°; ir 3180, 1670, 1605, 808, and 715 cm^{-1}; nmr (acetone-d_6) δ 1.20 (d, 6 H), 2.24 (s, 3 H), 3.03 (s, 1 H), 3.38 (m, 1 H), 6.87 (q, 2 H), 8.20 (s, 1 H), and 8.32 (s, 1 H).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.51; H, 7.92; N, 7.24.

4-Chloro-2-formamidophenol was crystallized from a mixture of benzene and petroleum ether: 74% yield; mp 156–157.5°; ir 3300, 3025, 1660, 1475, 1205, 1110, and 803 cm^{-1}; nmr (DMSO-d_6) δ 6.73 (s, 2 H), 8.03 (s, 1 H), 8.20 (s, 1 H), 9.45 (s, 1 H), and 9.83 (broad, 1 H).

Anal. Calcd for $C_7H_6NO_2Cl$: C, 49.00; H, 3.53; N, 8.16; Cl, 20.66. Found: C, 48.87; H, 3.70; N, 8.20; Cl, 20.77.

4- (or 6-) chloro-3,5-dimethoxy-2-formamidophenol, from 4,6-dimethoxysalicylaldehyde, was crystallized repeatedly from a mixture of benzene and cyclohexane: 17% yield; mp 145–146°; ir 3300, 3060, 1610, 1465, 1120, and 794 cm^{-1}; nmr (DMSO-d_6) δ 3.97 (s, 6 H), 6.50 (s, 1 H), 8.16 (s, 1 H), 8.50 (br, 1 H), and 9.50 (s, 1 H).

Anal. Calcd for $C_9H_{10}NO_4Cl$: C, 46.66; H, 4.35; N, 6.05; Cl, 21.15. Found: C, 46.86; H, 4.39; N, 6.17; Cl, 20.77.

Elemental analysis and the nmr spectrum of the reaction product after only two crystallizations indicated the presence of a mixture composed of chlorinated product (35%) and 3,5-dimethoxy-2-formamidophenol (65%). An attempt to prepare the unchlorinated material by use of excess aldehyde (2:1 molar ratio of aldehyde: NH_2Cl) gave a mixture of the two products (tlc). The chlorinated substance was isolated by repeated crystallization, but the other component was not cleanly separated.

4- (or 6-) chloro-3,5-dimethyl-2-acetamidophenol, obtained from 4,6-dimethyl-2-hydroxyacetophenone, was crystallized repeatedly from a mixture of benzene and petroleum ether: 22% yield; mp 179–181.5°; ir 3300, 3110, 1610, 1485, 1010, and 850 cm^{-1}; nmr (DMSO-d_6) δ 2.00 (s, 3 H), 2.10 (s, 3 H), 2.23 (s, 3 H), 6.67 (s, 1 H), 8.97 (s, 1 H), and 9.10 (s, 1 H).

Anal. Calcd for $C_{10}H_{12}NO_2Cl$: C, 56.21; H, 5.62; N, 6.55; Cl, 16.59. Found: C, 56.07; H, 5.71; N, 6.24; Cl, 16.33.

2-Hydroxy-4,6-dimethylacetophenone. A prior procedure[24] was used. Recrystallization from benzene gave a light yellow solid (10%), mp 57–57.5° (lit.[24] mp 57–58.5°).

o-Carvacrolaldehyde. A previous method[25] was used. Distillation provided a yellow liquid (12%): bp 81–84° (4 mm); nmr δ 12.20 (s, 1 H), 11.90 (s, 1 H), 7.09 (d, 1 H), 6.52 (d, 1 H), 3.44 (m, 1 H), 2.10 (s, 3 H), and 1.12 (d, 6 H).

o-Thymolaldehyde. A literature procedure[25] was used. Distillation gave a yellow liquid (10%): bp 79–80° (4 mm); nmr δ 12.20 (s, 1 H), 11.80 (s, 1 H), 6.43 (d, 1 H), 3.20 (m, 1 H), 2.39 (s, 3 H), 1.10 (d, 6 H).

5-Chlorosalicylaldehyde. Use of a published method[25] gave light yellow crystals (9% yield), mp 96–98° (lit.[25] mp 99°), from steam distillation.

N-Chloroacetophenonimine.[12] *N,N*-Dichloro-α-methylbenzylamine[26] (1.9 g, 0.01 mol) was added dropwise to a solution of potassium acetate (2.5 g, 0.025 mol) in absolute ethanol (13 ml) at reflux. The mixture was then refluxed for 30 min, cooled, and poured into water. After extraction with ether, the organic solution was dried and then freed of solvent, yielding 1.2 g (80%) of a yellow liquid. Titration with sodium thiosulfate indicated a purity of 83%; ir 3025, 1705, 1620, 1585, 758, and 692 cm^{-1}; nmr (CCl_4) δ 2.47 (s, 3 H) and 7.20–7.91 (m, 5 H).

Hydrolysis of 2-Acetamidophenol. 2-Acetamidophenol (5 g) was heated in concentrated HCl (50 ml) at reflux for 2 hr. After the mixture was cooled and neutralized with $NaHCO_3$, the crystals were collected, 1.1 g, mp 170–173° (lit.[20c] mp 174°). The ir spectrum was identical with that of an authentic sample of 2-aminophenol. The residual solution was evaporated to dryness and extracted with methanol. Removal of solvent from the dried solution provided 2 g of crude product.

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Registry No.—**1a,** 118-93-4; **1b,** 90-02-8; **2a,** 614-80-2; **2b,** 2843-27-8; **21,** 52260-17-0; **22,** 52260-18-1; **23,** 480-40-0; **24,** 480-41-1; monochloroamine, 10599-90-3; 1,8-dihydroxyanthraquinone, 117-10-2; 2-hydroxy-3-methoxybenzaldehyde, 148-53-8; 2,4-dimethoxy-6-hydroxybenzaldehyde, 708-76-9; 2-hydroxy-3-nitrobenzaldehyde, 5274-70-4; 1-formyl-2-naphthol, 708-06-5; o-benzoylphenol, 117-99-7; o-thymolaldehyde, 1666-00-8; o-carvacrolaldehyde, 1665-99-2; 2-hydroxy-4,6-dimethylacetophenone, 16108-50-2; 5-chlorosalicylaldehyde, 635-93-8; 2,2′-dihydroxyacetophenone, 17375-96-1; 2-formamido-6-methoxyphenol, 51029-17-5; 1-formamido-2-naphthol, 52260-19-2; 2-formamido-6-nitrophenol, 52260-20-5; 2-benzamidophenol, 3743-70-2; *N*-methyl-2-acetamidophenol, 573-27-3; 4-chloro-2-formamidophenol, 31354-50-4; 4- (or 6-) chloro-3,5-dimethoxy-2-formamidophenol, 52341-47-6; 3,5-dimethoxy-2-formamidophenol, 52260-21-6; 4- (or 6-) chloro-3,5-dimethyl-2-acetamidophenol, 52341-48-7; *N*-chloroacetophenonimine, 52260-22-7; *N,N*-dichloro-α-methylbenzylamine, 34863-18-8.

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