Table I. Physical, Analytical, and Spectral Properties

compd no.	R	yield, %	mp, °C	IR (KBr), cm^{-1}	NMR ($CDCl_3$), δ
3a	CH_2	19	182-184	1450 (s), 1370 (s), 1290 (s), 1250 (s), 1090 (s), 970 (s), 800 (s), 770 (s)	5.68 (s, 2 H), 7.70 (m, 8 H)
3b	$(CH_2)_2$	75	102-103	1450 (s), 1350 (s), 1250 (s), 1170 (m), 1110 (s), 1030 (s), 880 (s), 760 (s)	5.02 (s, 4 H), 7.65 (m, 8 H)
3c	$(CH_2)_3$	10	141-142	1470 (m), 1450 (m), 1370 (m), 1350 (m), 1270 (s), 1250 (s), 1100 (s), 1045 (s), 950 (s), 800 (m), 760 (s)	2.38 (t, 2 H, J = 5 Hz), 4.95 (t, 4 H, J = 5 Hz), 7.60 (m, 8 H)
3d	$(CH_2)_4$	82	89-91	1475 (m), 1445 (m), 1365 (m), 1275 (m), 1250 (s), 1100 (s), 1035 (m), 950 (s), 795 (m), 765 (s)	2.20 (m, 4 H, broad, 4.67 (m, 4 H, broad), 7.50 7.50 (m, 8 H)
3e	$(CH_2)_5$	73	65-66	1470 (m), 1450 (s), 1370 (s), 1280 (s), 1250 (s), 1110 (s), 970 (s), 880 (s), 770 (s)	1.93 (m, 6 H, broad), 4.60 (m, 4 H, broad), 7.50 (m, 8 H)
3f	$(CH_2)_6$	91	68-71	1450 (s), 1350 (s), 1270 (m), 1240 (s), 1100 (s), 1050 (s), 960 (s), 860 (s), 750 (s)	1.73 (m, 8 H, broad), 4.57 (m, 4 H, broad), 7.60 (m, 8 H)

to the corresponding dibromide as has been observed for other 1-alkoxy-1,2,3-benzotriazoles. A smaller shift is observed for **3a** due probably to the proximity of the halogens in dibromomethane as compared to the other dibromides.

In view of the excellent yields, except for **3a** and **3c** (for which multiple runs failed to alter the results), we are encouraged in our efforts to incorporate the benzotriazole nucleus as a backbone segment in a polymer system and in our investigation of the applicability of PTC to the synthesis of derivatives of 1-hydroxy-1,2,3-benzotriazole (**1**).

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 735B spectrometer. The NMR spectra were obtained on a Varian EM-360 spectrometer. The reaction of equimolar quantities of potassium hydroxide and 1-hydroxy-1,2,3-benzotriazole (**1**) in an aqueous solution followed by vacuum drying provided the potassium salt of 1-hydroxy-1,2,3-benzotriazole (**2**) which was used without further purification.

General Phase Transfer Catalyzed Alkylation Procedure. A mixture of **2** (0.02 mol), the appropriate dibromide (0.01 mol), tetrabutylammonium bromide (0.002 mol), and 50 mL of 1,2-dimethoxyethane was stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent removed under vacuum. The products were recrystallized from methanol. Properties of all new compounds are summarized in Table I.

Registry No. **2**, 62244-77-3; **3a**, 83615-76-3; **3b**, 83615-77-4; **3c**, 83615-78-5; **3d**, 83615-79-6; **3e**, 83615-80-9; **3f**, 83615-81-0; TBAB, 1643-19-2.

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Synthesis and Spectroscopic Data of Chlorinated 4-Hydroxybenzaldehydes

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All chlorinated 4-hydroxybenzaldehydes including three hitherto unknown compounds have been synthesized from chlorinated phenols by applying the Reimer-Tiemann method. ^1H NMR, ^{13}C NMR, and mass-spectral data on all compounds are reported.

In connection with our interest in chlorinated phenolic compounds occurring in pulp bleach liquors we recently had need of some chlorinated aromatic aldehydes. We now wish to report on the synthesis and spectroscopic properties of chlorinated 4-hydroxybenzaldehydes (see Figure 1). Some of them

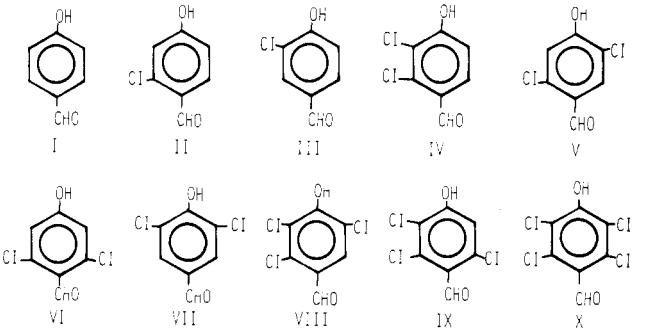

Figure 1. Structures and notation of compounds studied.

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Table I. Properties of 4-Hydroxybenzaldehyde (I) and Its Chloro Derivatives (II–X)

compd no.	mp, °C	yield, %	chemical shifts, ppm: ^{1}H NMR[b]	^{13}C NMR
I[a]	115–117		6.8–8.0 (m, 4 H), 9.4 (broad s, OH), 9.86[c] (t, 1 H)	116.5, 130.3, 132.7, 163.8, 191.0
II	146–147[d]	10	6.8–7.9 (m, 3 H), 9.8 (broad s, OH), 10.24[c] (d, 1 H)	116.0, 117.5, 126.0, 132.1, 139.7, 164.1, 188.0
III	133–134[e]	12	7.1–8.0 (m, 3 H), 9.7 (broad s, OH), 9.85[c] (d, 1 H)	117.8, 122.1, 130.8, 131.2, 132.2, 159.1, 190.2
IV	184–185[f]	14	7.0–7.9 (q, 2 H), 10.25[c] (d, 1 H), 10.3 (broad s, OH)	115.9, 121.1, 127.2, 129.5, 137.9, 160.3, 188.3
V	159–160	8	7.15 (s, 1 H), 7.81 (s, 1 H), 10.18 (s, 1 H), 10.2 (broad s, OH)	118.5, 121.6, 126.5, 131.4, 137.5, 159.4, 187.4
VI	223–225[g]	10	6.99[c] (d, 2 H), 10.2 (broad s, OH), 10.34[c] (d, 1 H)	117.9, 122.5, 139.1, 162.8, 187.4
VII	156–157[h]	8	7.88 (s, 2 H), 9.70 (broad s, OH), 9.86 (s, 1 H)	123.3, 130.5, 130.7, 155.0, 189.5
VIII	164–165	10	7.80 (s, 1 H), 8.5 (broad s, OH), 10.23 (s, 1 H)	122.0, 122.7, 127.1, 129.0, 136.1, 155.8, 187.3
IX	178–179	5	7.15[c] (d, 1 H), 10.3[c] (d, 1 H), 10.4 (broad s, OH)	117.8, 121.6, 124.2, 136.4, 137.1, 158.6, 187.5
X	203–205	11	9.4 (broad s, OH), 10.32 (s, 1 H)	122.0, 125.5, 134.5, 154.7, 187.4

[a] Commercial product. [b] The broad range, the lowest-field absorptions of aromatic protons. The higher-field absorptions are hydroxyl and formyl protons. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, H = number of protons (integrated) corresponding to the particular absorptions. [c] Mean value of absorptions. [d] Literature (*7*) mp 146.2–146.9 °C. [e] Literature (*9*) mp 132–134.5 °C. [f] Literature (*1*) mp 184–185 °C. [g] Literature (*3*) mp 223.5–224.5 °C. [h] Literature (*10*) mp 157–158 °C.

Table II. Relative Intensity of Characteristic Ions in the Mass Spectra of I–X[a]

	m/z (relative intensity, %)[b]									
	I[c]	II	III	IV	V	VI	VII	VIII	IX	X
$[M]^{+\cdot}$	122 (90.5)	156 (60.1)	156 (67.5)	190 (56.4)	190 (57.8)	190 (47.6)	190 (52.1)	224 (54.5)	224 (50.9)	258 (38.3)
$[M - H]^+$	121 (100)	155 (100)	155 (100)	189 (100)	189 (100)	189 (100)	189 (100)	223 (100)	223 (100)	257 (74.6)
$[M - H - CO]^+$	93 (52.4)	127 (21.9)	127 (30.1)	161 (7.0)	161 (14.4)	161 (9.5)	161 (7.8)	195 (4.2)	195 (5.3)	229 (3.0)
$[M - H - CO - CO]^+$	65 (39.5)	99 (35.0)	99 (41.9)	133 (31.0)	133 (23.8)	133 (29.3)	133 (29.8)	167 (13.4)	167 (23.1)	201 (15.2)
$[M - H - CO - Cl]^{+\cdot}$		92 (9.3)	92[d] (4.9)	126 (12.5)	126 (11.4)	126 (10.4)	126 (11.1)	160 (6.7)	160 (11.1)	194 (8.1)
$[M - H - CO - CO - C_2H_2]^+$	39 (32.8)	73 (28.2)	73 (29.2)	107 (5.6)	107 (5.1)	107 (7.8)	107 (7.8)	141 (1.2)	141 (0.8)	
$[M - H - CO - CO - HCl]^+$		63 (50.6)	63 (59.7)	97 (22.0)	97 (33.0)	97 (28.8)	97 (22.3)	131 (8.0)	131 (12.0)	165 (7.7)

[a] See Figure 1. [b] Ions containing ^{37}Cl are not shown. [c] Mass spectrum and most characteristic fragments presented in ref *11*. [d] $[M - H - CO - HCl]^+$, 91 (15.0).

have been previously used as substrates in the synthesis of diuretic, antihypertensive, and psychotropic drugs (*1*–*4*). Recently, 4-hydroxybenzaldehyde (I) and its chloroderivative VII have also been shown to be present in kraft black and Canadian kraft spent bleach liquor (*5*, *6*).

When the Reimer–Tiemann reaction with chlorinated phenols was repeated by applying the procedure described previously (*7*), three hitherto unknown chlorinated aldehydes (VIII–X) were formed. The yields of products varied from about 5% to 15% depending on the substitution of the substrate in each synthesis. The results of the synthesis and spectroscopic data (^{1}H NMR, ^{13}C NMR, and mass spectra) are given in Tables I and II.

Experimental Section

All melting points were taken in open capillaries and are uncorrected. NMR spectra were recorded on a JEOL FX-60 FT spectrometer for ~10% acetone-d_6 solutions; the chemical shifts are described as parts per million (ppm) from tetramethylsilane. The spectral widths in ^{1}H and ^{13}C NMR experiments were 800 Hz and 4 KHz, respectively. In ^{13}C NMR experiments, the flip angle was 45° and pulse repetition times of 2.0–10.0 s were applied, depending on the relaxation rates of the measured resonances. Mass spectra were run on a Varian MAT-212 mass spectrometer operating at 70 eV and using the direct inlet. The purity of compounds was also checked by glass capillary gas chromatography; the column used was a SE-30 (25 m × 0.22 mm i.d.) quartz capillary column and the instrument was a Perkin-Elmer Sigma 3 gas chromatograph fitted with a flame ionization detector.

General Procedure for the Preparation of II–X. Chloroform (0.175 mol) was added dropwise to a mixture of $Ca(OH)_2$ (0.378 mol), Na_2CO_3 (0.302 mol), chlorophenol substrate (0.088 mol), H_2O (200 mL) at 70 °C over a 0.5-h period. The mixture was refluxed for 2 h and after being cooled was acidified (to pH ~2) with concentrated HCl. The product was steam distilled until all unreacted chlorophenol and chlorosalicylaldehyde residues had been removed from the reaction mixture. This was checked by analyzing the concentrated distillate by glass capillary gas chromatography after derivatization of the sample with acetic anhydride (*8*) and also by ^{1}H NMR spectroscopy. After the solution was cooled to about 0 °C and allowed to stand for 12 h, the 4-hydroxybenzaldehyde derivative in the steam-distillation flask was filtered, dissolved in CCl_4, and treated with decolorizing charcoal. After this solution was cooled, the precipitate formed was filtered, recrystallized twice from CCl_4, and finally sublimated at 0.5 mm at 180–200 °C.

Registry No. I, 123-08-0; II, 56962-11-9; III, 2420-16-8; IV, 16861-22-6; V, 27164-10-9; VI, 60964-09-2; VII, 2314-36-5; VIII, 83016-58-4; IX, 83016-59-5; X, 83016-60-8; *m*-chlorophenol, 108-43-0; *o*-chlorophenol, 95-57-8; 2,3-dichlorophenol, 576-24-9; 2,5-dichlorophenol, 583-78-8; 3,5-dichlorophenol, 591-35-5; 2,6-dichlorophenol, 87-65-0; 2,3,6-trichlorophenol, 933-75-5; 2,3,5-trichlorophenol, 933-78-8; 2,3,5,6-tetrachlorophenol, 935-95-5.

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