# 1,3-DIHYDROXYBENZENE-2-$^{13}$C: ITS PREPARATION AND REACTION WITH CHLORINE AND BROMINE IN AQUEOUS SOLUTION

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## SUMMARY

1,3-cyclohexanedione-2-$^{13}$C was prepared by intramolecular Claisen condensation of methyl 5-oxohexanote-6-$^{13}$C with sodium methoxide. Formation of the ketoester starting material involved treatment of a mixed dicarboxylic anhydride with an isotopically-labelled Grignard reagent, methyl-$^{13}$C magnesium iodide. Dehydrogenation of carbon-13 labelled cyclohexanedione over a palladium/carbon catalyst produced 1,3-dihydroxybenzene-2-$^{13}$C. Chlorination and bromination of dihydroxybenzene in aqueous solution yielded isotopically-labelled chloroform and bromoform, each having enriched carbon-13 contents equivalent to that of the organic substrate.

Key Words: Resorcinol, Grignard Reaction, Claisen Condensation, Catalytic Dehydrogenation, Halogenation, Trihalomethanes.

## INTRODUCTION

Carcinogenic trihalomethane pollutants, such as chloroform ($CHCl_3$) and bromo-bromoform ($CHBr_3$) are frequently produced in low concentration during the disinfection of water with chlorine (1). It has been well-documented that these species arise from the chlorination reactions of humic substances, dissolved in

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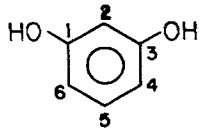
most natural waters (2-6). Humic material itself, however, is of highly variable chemical composition. Therefore, considerable attention has recently been directed to the study of benzenediols as simple model compound systems for the reactive phenolic structure of naturally-occurring organic matter (7-9). Derivatives of 1,3-dihydroxybenzene (resorcinol), which undergo rapid reaction with chlorine in weakly alkaline solution (pH 8-10) to give nearly quantitative yields of $CHCl_3$ (10,11), have been used extensively for this purpose.




Although chloroform is the primary reaction product of the chlorination of model compounds and humic acid under most experimental conditions, the mechanism of reaction even with simple substrates such as resorcinol is poorly understood. For example, the pH-dependence of $CHCl_3$ formation does not appear to conform to the commonly accepted haloform mechanism first proposed by Rook (7,8). In addition, a variety of other Cl-containing products are formed during this reaction. The yields of these species depend strongly on pH and the molar ratio of $Cl_2$ to substrate. Christman and coworkers (4,9) and Boyce and Hornig (10,11) have studied these reactions in considerable detail and have concluded that a number of parallel reaction pathways are likely.

A review of the available literature showed that early studies of the mechanism of the chlorination of 1,3-dihydroxybenzenes were conducted under more vigorous reaction conditions than those encountered in typical water treatment processes (12,13). Nevertheless, the results of these investigations suggest that electrophilic incorporation of Cl followed by hydrolysis about the $C_2$-carbon center of the aromatic ring are salient features in the conversion of derivatives of resorcinol to chloroform under milder conditions. Rook (7,8) has proposed that $CHCl_3$ originates from the $C_2$-site of 1,3-dihydroxybenzene. Experimental data obtained in our laboratory (10,11) appear to support this assertion.

The synthesis of isotopically-labelled resorcinol was undertaken as an in-

tegral part of the current investigation of the halogenation of 1,3-dihydroxybenzene in dilute solution. This paper describes in detail the preparation of 1,3-dihydroxybenzene-2-$^{13}C$. Chlorination and bromination of $^{13}C$-resorcinol produced a variety of $^{13}C$-substituted organohalide reaction products which were characterized by combined gas chromatography/mass spectrometry.

## EXPERIMENTAL PROCEDURE

### Synthesis of 1,3-Dihydroxybenzene-2-$^{13}C$

The synthetic scheme utilized for the preparation of 1,3-dihydroxybenzene-2-$^{13}C$ is summarized in Figure 1. The procedure involved the cyclization of methyl 5-oxohexanote-6-$^{13}C$ (4). The ketoester starting material was prepared by a Grignard reaction of the mixed dicarboxylic anhydride 3 with methyl-$^{13}C$ magnesium iodide, $^{13}CH_3MgI$. Anhydride 3 was formed by treatment of o-methoxybenzoic acid (1) with methyl 4-(chloroformyl)butyrate (2) in the presence of triethylamine, $Et_3N$. The isotopically-labelled Grignard reagent was generated from iodomethane-$^{13}C$, $^{13}CH_3I$. An intramolecular Claisen condensation reaction of ketoester 4 with sodium methoxide ($NaOCH_3$) yielded 1,3-cyclohexanedione-2-$^{13}C$ (6). Dehydrogenation of the labelled cyclohexanedione over a palladium-carbon catalyst (Pd/C) produced the desired 1,3-dihydroxybenzene-2-$^{13}C$ (7).

### Methyl 5-oxohexanote-2-$^{13}C$ (4)

Methyl 5-oxohexanoate 6-$^{13}C$ (4) was prepared from the method of Terasawa and Okada (14). The reaction was carried out under an atmosphere of dry nitrogen ($N_2$) using a 1 L three-neck round-bottom flask fitted with a 125 ml addition funnel. A solution of methyl 4-(chloroformyl)butyrate (2) (Aldrich) (18.4 g, 0.112 mol) in 100 ml dry tetrahydrofuran (THF: Fisher reagent dried over Woelm activity I basic alumnia) was added dropwise to a cold (-10°C), stirred mixture of o-methoxybenzoic acid (1) (Aldrich) (17.0 g, 0.112 mol) and triethylamine (Eastman) (11.3 g, 0.122 mol) in 500 ml THF. The addition required 30 min and the reaction mixture was stirred for an additional 30 min after complete introduction of the methyl 4-(chloroformyl)butyrate solution. Anhydride 3 formed as a

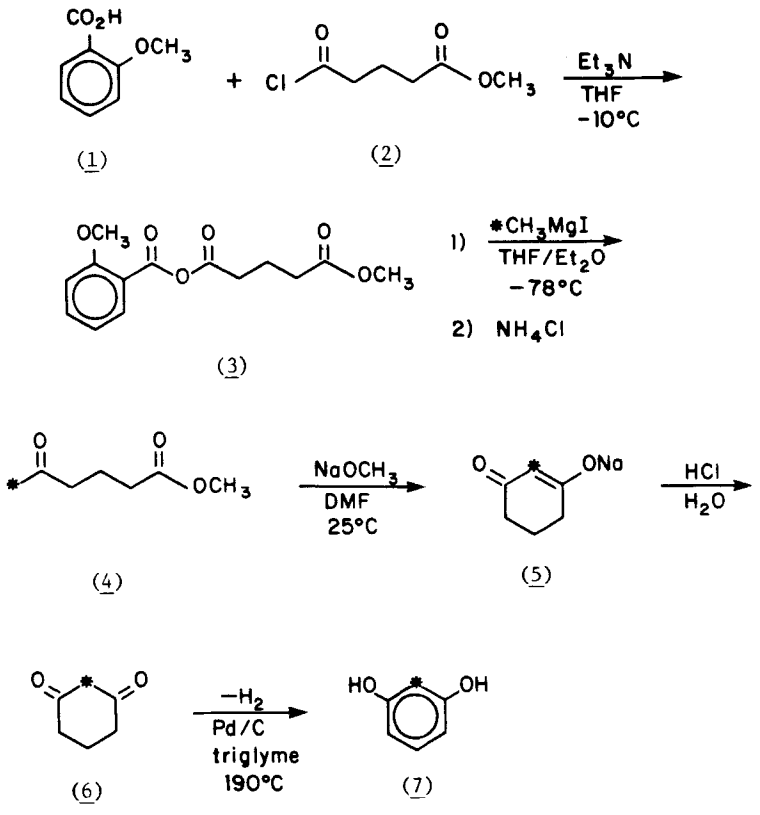



Fig. 1. Synthetic scheme utilized for the preparation of 1,3-dihydroxybenzene-2-$^{13}C$ (* ≡ $^{13}C$).

white precipitate suspended in the reaction mixture.

The ether solution of $^{13}CH_3MgI$ was prepared using a standard procedure (15). A solution of $^{13}CH_3I$ (20 g, 0.141 mol) (consisting of 5 g $^{13}CH_3I$ (Stöhler) and 15 g unlabelled $CH_3I$), in 40 ml dry ether, was added dropwise to magnesium metal.

After cooling of the anhydride reaction mixture to -78°C, a solution of $^{13}CH_3MgI$ (18.6 g, 0.112 moles) in 20 ml dry ether (Fisher anhydrous) was introduced dropwise to the stirred suspension of anhydride 3 over the course of 45 min. Stirring was continued at -78°C for 30 min subsequent to addition of the Grignard reagent. The mixture was allowed to warm slowly to room temperature and the reaction products were formed upon hydrolysis with 200 ml of 10% $NH_4Cl$(aq). The ether/THF layer was retained and combined with additional ether extracts

(100 ml and 25 ml) of the aqueous component. The combined solvent extracts were washed successively with 1 M $Na_2CO_3$(aq) (2 x 100 ml)and saturated aqueous NaCl (2 x 100 ml) and then dried over anhydrous $Na_2SO_4$.

The experimental procedure was repeated twice and the crude product from each reaction was combined. Preparative column chromatography on silica gel (Davison: 60-200 mesh; 1:5 ether/hexane eluent) gave 15.6 g of a clear liquid. Distillation under reduced pressure (90-92°C, 20 mm Hg) produced 13.5 g (30% yield of pure methyl 5-oxohexanoate-6-$^{13}C$ (4). The IR, UV, NMR ($^1H$ and $^{13}C$) and mass spectra were identical to data recorded from a genuine sample of unlabelled keto-ester prepared by esterification of 5-oxohexanoic acid with boron trifluoride-etherate according to the procedure of Kadaba (16). Comparison of the mass spectrum with data reported by Williams and Howe (17) provided further confirmation of the product structure. IR(liquid): 2960(s), 1670(s) (ester C = 0), 1660(s) (ketone C = 0), 1440(s), 1370(s)$cm^{-1}$; UV (MeOH):270, 277 (sh) nm; $^1H$ NMR ($CDCl_3$): δ3.67(s), 3.20(s), 2.62-1.60(m), 2.15(s), 1.07(s) ppm (relative to TMS): $^{13}C$ NMR ($CDCl_3$): δ207.6, 173.3, 51.4, 42.3, 32.9, 29.7 ($C_6$ enhanced intensity showing $^{13}C$-enrichment), 18.8 ppm (relative to TMS); MS: m/e 144 ($[M]^+$), m/e 74 ($[M-70]^+$), m/e 59 ($[M-85]^+$), m/e 43 ($[M-101]^+$) enhanced relative abundance of m/e 44 indicates $^{13}CH_3CO^+$).

1,3-Cyclohexanedione-2-$^{13}C$ (6)

The cyclization of methyl 5-oxohexanoate-6-$^{13}C$ (4) was performed using a procedure described by Mueller (18). To a 100 ml round-bottom flask containing a stirred suspension of $NaOCH_3$ (2.2g, 0.041 mol) (freshly prepared from methanol (Fisher Spectranalyzed) and sodium metal) in dry dimethylformamide (DMF: Fisher reagent, distilled from CaO under reduced pressure) was added dropwise a solution of ketoester 4 (5.9 g, 0.041 mol) in 15 ml DMF. The addition was carried out using a 25 ml addition funnel, over the course of 30 min. The reaction was carried out under an atmosphere of dry $N_2$. After stirring for 90 min, removal of the solvent under vacuum yielded a pale yellow solid. The crude product, the sodium enolate of 1,3-cyclohexanedione-2-$^{13}C$ (5), was purified by grinding the solid to a fine powder and heating in 100 ml ether under reflux for

8 hr. Filtration gave a white solid (4.5 g, wet) which was dried in the air for several hours.

Dissolution of the purified enolate salt in 7 ml water and acidification of the solution by dropwise addition of 3 ml concentrated HCl effected crystallization of the product diketone 6 . After cooling to -10°C, filtration yielded 2.8 g (61% yield)of 1,3-cyclohexanedione-2-$^{13}$C.(m.p. 103-104°C from $C_6H_6$). IR, UV, NMR ($^1$H and $^{13}$C) and mass spectral data matched measurements obtained from a commercial sample of unlabelled 1,3-cyclohexanedione (Aldrich). Comparison with published spectra (19) provided further confirmation of the product structure. IR(KBr): 2960(s), 1640(s), 1540(s), 1460(s), 1390(s), 1320(s), 1270(s), 1240(s), 1180(s), 1150(s)cm$^{-1}$; UV (MeOH): 254 nm; $^1$H NMR ($CDCl_3$) δ9.79(s), 7.27(s), 5.56(s), 3.24(s), 2.8-1.5(m) ppm (relative to TMS); $^{13}$C NMR ($CDCl_3$): δ203.8, 192.3, 104.2 ($C_2$ enhanced intensity showing $^{13}$C-enrichment), 39.7, 32.2, 21.0 ppm; MS (solid probe): m/e 112 ($[M]^+$), m/e 84 ($[M-28]^+$), m/e 70 ($[M-42]^+$), m/e 55 ($[M-57]^+$), m/e 42 ($[M-70]^+$, base peak).

This reaction was repeated using the remaining ketoester 4. Finally, additional 1,3-cyclohexanedione-2-$^{13}$C was isolated through extraction of the acidified filtrate from the final step of each reaction with methylene chloride.

1,3-Dihydroxybenzene-2-$^{13}$C (7).

A modification of a published procedure was employed (20). Attempted dehydrogenation of crude 1,3-cyclohexanedione-2-$^{13}$C produced a complex mixture of products composed primarily of 3-isopropoxyphenol and a low yield of resorcinol. This result was attributed to contamination of the diketone with residual acid from the previous crystallization step. Therefore, rigorous purification of dione 10 was undertaken.

Crude 1,3-cyclohexanedione-2-$^{13}$C (1.07 g, 9.55 mmol) was recrystallized three times from benzene ($C_6H_6$) to yield 0.68 g of a white solid. Acidic impurities were removed by dissolution of the recrystallized product in 20 ml methylene chloride (Fisher) and stirring for several minutes over 0.5 g $NaHCO_3$ and 0.5 g $Na_2CO_3$ (Fisher). After filtration, evaporation of the solvent under $N_2$ left a white residue upon which recrystallization from $C_6H_6$ yielded 0.57 g of pure

1,3-cyclohexanedione-2-$^{13}C$.

To a 50 ml round-bottom flask containing a hot (190°C) (oil bath), stirred suspension of 0.30 g 10% Pd/C (Alfa) in 25 ml triglyme (Tridöm-Fluka: distilled from $LiAlH_4$) was added dropwise a solution of 0.57 g of purified 1,3-cyclohexanedione-2-$^{13}C$ (6) in 10 ml dry 2-propanol (Fisher: distilled from magnesium isopropoxide). The addition required one hour and was carried out under a $N_2$ atmosphere. During the reaction, the volatilized 2-propanol was removed by distillation through a condenser. The reaction mixture was stirred for an additional 30 min at 190°C and then allowed to cool to room temperature. After dilution with 50 ml anhydrous ether, the unreacted catalyst was removed via filtration. The product was extracted from the ethereal solution with 20% NaOH (4 x 5 ml). The aqueous layer was retained, acidified to pH 2 (indicator paper) with concentrated HCl and cooled to 0°C (ice-bath). Isolation of the product was achieved by extraction with ether (3 x 25 ml). Evaporation of the solvent under vacuum gave 10 ml of a solution which was concentrated further under a stream of $N_2$. The residue, a red oil, crystallized on standing. Recrystallization from $C_6H_6$ and then $CHCl_3$ yielded 0.26 g (45% yield) of pure 2-$^{13}C$ 1,3-dihydroxybenzene (7) (white crystals, m.p. 108-109°C; mixed m.p. with resorcinol, 108-109.5°C). Analysis by IR, NMR ($^1H$ and $^{13}C$) and mass spectrometry produced spectra identical to data collected from a commercial sample of unlabelled resorcinol (Fisher) as well as published measurements (21).

IR (KBr): 3230(s), 1610(s), 1490(s), 1300(s), 1150(s), 960(s)$cm^{-1}$; $^1H$ NMR ($d^6$-acetone): δ8.11(s), 7.12-6.84 (m), 6.43-6.21(m) ppm (relative to TMS); $^{13}C$ NMR (acetone-$d^6$) (see Figure 2): δ159.4, 130.5, 107.5, 103.4 ($C_2$, enhanced intensity showing $^{13}C$-enrichment) ppm; MS (see Figure 3) (solid probe): m/e 110 ($[M]^+$, base peak).

Chlorination and Bromination of 1,3-Dihydroxybenzene-2-$^{13}C$

The procedure for the halogenation of resorcinol-2-$^{13}C$ was identical to that described previously by Boyce and Hornig (10,22) for the reactions of unlabelled polyhydroxyaromatic and diketone compounds. Chlorination of a $5x10^{-4}$ M substrate solution was carried out at pH 4, 7 and 10 with a five- and ten-fold molar excess

of $Cl_2$ (added as NaOCl). A $1x10^{-4}$ M resorcinol solution was employed in the experiments with bromine due to the lower solubility of $Br_2$ (relative to chlorine) in water. The experiments were carried out at 10°C and constant pH was maintained during the reactions through the use of 0.2 M phosphate buffers. After 3 hr, residual halogen was removed by addition of excess sodium sulfite. The solution was acidified to pH 1 and the reaction products were extracted from aqueous solution with ether. The extracts were concentrated to < 2 ml, prior to GC/MS analysis, by evaporation of the solvent under vacuum.

Analysis of Reaction Products

Ultraviolet spectra were recorded on a Perkin-Elmer Model 571 UV/VIS spectrophotometer. Infrared spectra were measured using a Perkin-Elmer Model 599 IR spectrophotometer. The $^{1}H$ and $^{13}C$ nuclear magnetic resonance data were collected on a JEOL FX 60Q Fourier Transform NMR spectrometer.

Mass spectra were obtained with a Finnigan Series 4000 mass spectrometer interfaced to a Finnigan Model 9610 gas chromatograph. Samples were introduced to the mass spectrometer by direct probe insertion to the ion source or after chromatographic separation on 6 ft x 0.25 in o.d. glass GC columns packed with either 3% SP-2100 or 10% SP-1000 on Supelcoport (Supelco). Electron impact mass spectra were recorded at an ionization energy of 70 eV. Data acquisition and analysis were performed using a Data General Nova 3 minicomputer programmed with the Finnigan/INCOS software system.

## RESULTS AND DISCUSSION

Synthesis of 1,3-Dihydroxybenzene-2-$^{13}C$

The structure of 1,3-dihydroxybenzene-2-$^{13}C$ was assigned through a comparison of the product spectra with data recorded from an authentic sample of unlabelled resorcinol. The UV, IR, and $^{1}H$ NMR data for the $^{13}C$-enriched product and $^{12}C$-resorcinol were identical. The relative abundance of the $[M+1]^{+}$ peak, i.e., the ratio of intensities of m/e 111 to m/e 110, in the mass spectrum of isotopically-labelled dihydroxybenzene is 21% greater than that detected in the spectrum of

the unlabelled benzenediol. The $^{13}C$ NMR data also showed the enrichment expected as indicated by the enhanced intensity of the peak at δ103.4. We have assigned this resonance frequency to the $C_2$-aromatic carbon center on the basis of results reported by Mukoyama and coworkers (23).

Chlorination and Bromination of 1,3-Dihydroxybenzene-2-$^{13}C$

At pH 4, 7 and 10, treatment of resorcinol-2-$^{13}C$ with a ten-fold molar excess of $Cl_2$ and $Br_2$ yielded $^{13}CHCl_3$ and $^{13}CHBr_3$. The trihalomethane products were identified by gas chromatography/mass spectrometry (GC/MS). Confirmation of each product identity was obtained through a comparison of the sample chromatographic retention time with measurements recorded using authentic chloroform or bromoform standards. The $^{13}C$-enrichment of the isotopically-labelled haloform products was equivalent, within experimental error (±5%), to that of the dihydroxybenzene substrate (Table I). This result demonstrates unambiguously that at least 95% of the $CHCl_3$ and $CHBr_3$ originates from the $C_2$-site of the aromatic ring.

Several other $^{13}C$-substituted reaction products were also detected in addition to $^{13}CHCl_3$ from the chlorination of isotopically-labelled resorcinol. For example, the reaction of 1,3-dihydroxybenzene-2-$^{13}C$ with hypochlorite in neutral solution ($[Cl_2]/[Substrate] = 5$) yielded 2,4,6-trichloro-1,3-dihydroxybenzene-2-$^{13}C$ (8) and a product which we have tentatively assigned the structure 3,5,5-trichlorocyclopent-3-ene-1,2-dione-5-$^{13}C$ (9). The corresponding unlabelled diketone 10 has been isolated in pure form (<0.1% yield based on resorcinol) in our laboratory from analogous experiments with unlabelled 1,3-dihydroxybenzene (24).

Christman and coworkers (9) have tentatively identified 3,5,5-trichlorocyclopent-3-ene-1,2-dione (10) as the major intermediate formed *in addition to chloroform* from the chlorination of the unlabelled resorcinol at pH 7. Rook (8) has also observed the formation of this species. The current findings indicate that the labelled diketone 9 is formed either as a precursor to $^{13}CHCl_3$ or from a reaction pathway in competition with that leading to chloroform.

Chlorination of 1,3-dihydroxybenzene-2-$^{13}C$ at pH 4 also yielded trichloroacetic acid-2-$^{13}C$ (detected as the corresponding methyl ester after derivatization with $BF_3$/methanol). Boyce and Hornig (10,11) have shown that the reactions of

Table I. Carbon-13 enrichment of isotopically-labelled resorcinol and halogenated reaction products[a]

| COMPOUND | pH | % $^{13}C$ |
|---|---|---|
| 1,3-dihydroxybenzene-2-$^{13}C$[b] | - | 21 |
| $^{13}CHCl_3$[c] | 4 | 22 |
| | 7 | 20 |
| | 10 | 23 |
| $^{13}CHBr_3$[d] | 4 | 22 |
| | 7 | 25 |
| | 10 | 23 |
| 3,5,5-trichlorocyclopent-3-ene-1,2-dione-5-$^{13}C$ (9)[e] | 7 | 24 |

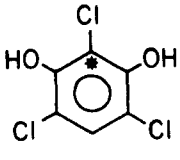
[a]Carbon-13 content calculated from mass spectral measurements. Reported values denote $^{13}C$-enrichment after subtraction of natural $^{13}C$ isotopic abundance as determined from the mass spectrum of the corresponding unlabelled compound.

[b]Calculated from parent ion: $[M+1]^+/M^+$ i.e., Relative Intensity (m/e 111/ m/e 110)

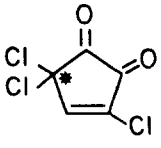
[c]Calculated from $CHCl_2^+$ fragment ion: Relative Intensity (m/e 84/ m/e 83)

[d]Calculated from $CHBr_2^+$ fragment ion: Relative Intensity (m/e 172/ m/e 171)

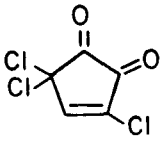
[e]Calculated from parent ion: Relative Intensity (m/e 199/ m/e 198)




(8)




(9)




(10)

several unlabelled 1,3-dihydroxyaromatic substrates also proceed under acidic and neutral conditions to give labile trichloromethyl-substituted compounds such as trichloroacetate, pentachloroacetone and trichloroacetaldehyde (chloral). These species decomposed to $CHCl_3$ during direct aqueous injection gas chromatographic analysis of the reaction solutions. The identification of $Cl_3{}^{13}CCO_2H$ suggests that the pathways of formation of such $CCl_3$-substituted species also involve degradation of the aromatic ring at the $C_2$-position of 1,3-dihydroxybenzene.

These results are consistent with the general reaction scheme summarized in

Figure 2. The pathway is based on the observations reported previously by Rook (7,8). Initial halogenation of the substrate yields 2,4,6-trichloro-1,3-dihydroxybenzene, which decomposes via a complex series of steps, perhaps involving cyclohexenedione intermediates 11 and 12, to give species such as the chlorinated alkenone 13. Further incorporation of chlorine and hydrolysis would readily convert this intermediate to $CHCl_3$ under neutral and alkaline conditions.

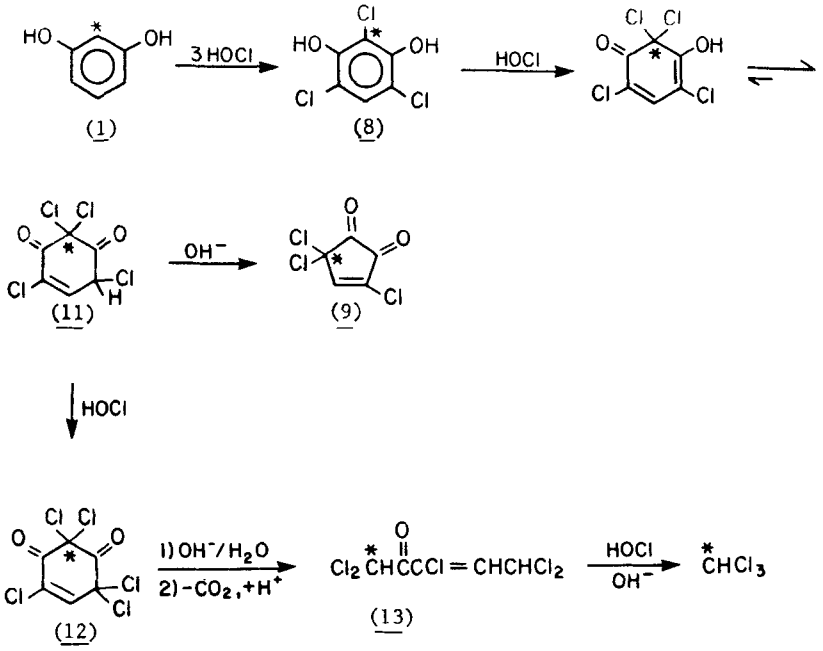
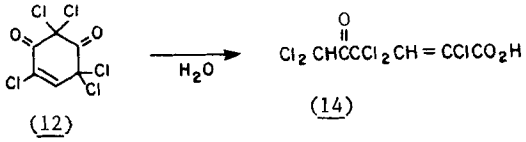
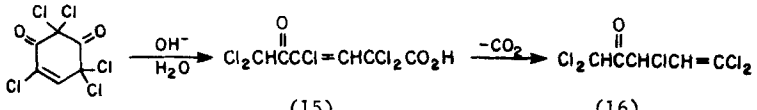



Figure 2. Proposed reaction pathway for the formation of chloroform from the chlorination of 1,3-dihydroxybenzene-2-$^{13}C$ (* ≡ $^{13}C$).

Zincke (12) first observed that treatment of resorcinol with $Cl_2$ in chloroform solvent produced 2,2,4,4,6-pentachlorocyclohex-3-ene-1,3-dione (12). This compound was unstable upon dissolution in water and underwent hydrolysis to form 2,4,4,6,6-pentachloro-5-oxo-hex-2-enoic acid (14) (Equation 1). Moye (13) has reinvestigated the decomposition of pentachlororesorcinol in aqueous solution and identified the pentachloro-unsaturated ketone 16 as the primary hydrolysis product (Equation 2).




(12) (14) (1)




(12) (15) (16) (2)

Analysis by GC/MS detected compounds with mass spectra consistent with derivatives of structures 13 and 14 from the chlorination of a variety of unlabelled 1,3-dihydroxybenzenes under acidic, neutral and alkaline conditions (10,11,22). In the proposed scheme, 3,5,5-trichlorocyclopent-3-ene-1,2-dione is formed via a route which diverges from the primary pathway of $CHCl_3$ production.

While the results obtained from the experiments with isotopically-labelled resorcinol do not permit an evaluation of the exact sequence of steps involved in $CHCl_3$ production, they lend further support to a general mechanistic scheme such as that outlined in Figure 2. The decomposition of trichlororesorcinol to form $CHCl_3$, the trichlorocyclopentenedione 9, and the unlabelled analogs of intermediates such as 13 and 15 has been confirmed in separate experiments with genuine 2,4,6-trichloro-1,3-dihydroxybenzene. Bromination of resorcinol at low $[Br_2]$/[Substrate] ratios also gave mono-, di- and tribomo-substitution products. This observation, coupled with the identification of $^{13}CHBr_3$, provides additional evidence that similar pathways govern the reaction of 1,3-dihydroxybenzenes with both chlorine and bromine in dilute aqueous solution.

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