# 1,4-Benzodioxin-2(3*H*)-one and Some of its Derivatives



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The methods of synthesis of 1,4-benzodioxin-2(3*H*)-one have been reexamined. Frequently quoted in the literature the method of Ghosh has been found to give impure (2-hydroxyphenoxy)acetic acid rather than the lactone. Using various methods some simple derivatives of the title lactone substituted in the benzene ring have been prepared and characterized. The bromination of the lactone with NBS gives predominantly 7-bromo-1,4-benzodioxin-2(3*H*)-one under electrophilic conditions, while 6-bromo-1,4-benzodioxin-2(3*H*)-one is obtained as a major isomer under photolytic conditions.

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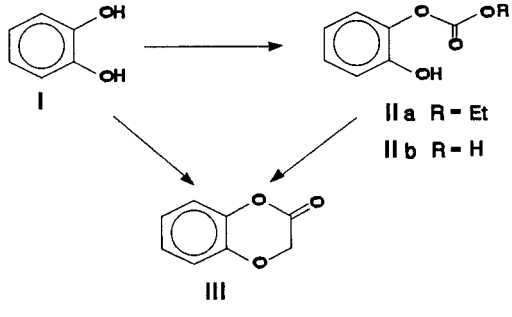
In the course of our study on the reactivity of unsymmetrical 1,4-benzodioxins [1] we became interested in a system of 1,4-benzodioxin-2(3*H*)-one **III** and its derivatives. This system is found in some naturally occurring compounds such as caleteucrins and calefoliones which were isolated from various parts of *Calea* species [2]. Another secondary metabolite containing this system, 3-methylidene-6-methoxy-1,4-benzodioxin-2-one, has been extracted from the fungus *Mycosphaerella ligulicola* [3]. The most recent natural product possessing system **III** that has been reported is phytoalexin yurinelide, which has been isolated from lily bulbs (*Lilium maximowiczii*) infected with *Fusarium oxysporum*, a fungus causing basal rot [4].

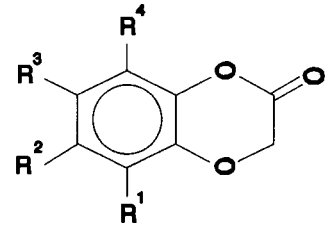
1,4-Benzodioxin-2(3*H*)-one **III** has been reported by Carter and Lawrence as a product of distillation of both (2-hydroxyphenoxy)acetic acid **IIb** and ethyl (2-hydroxyphenoxy)acetate **IIa** [5] and later by Ghosh as a product of the acid catalyzed hydrolysis of ethyl (2-hydroxyphenoxy)-acetate **IIa** giving the lactone **III** *via* hydroxyacid **IIb** [6]. Sprecker and co-workers [7] have patented **III** as one of the compounds enhancing the aroma and taste of foodstuffs. They obtained it in the reaction of catechol **I** with bromoacetyl bromide in the presence of triethylamine (Scheme 1).

Scheme 1




There are few reports which describe the synthesis of derivatives of **III** that contain substituents in the aromatic ring. Preparation of 6,8-di-*tert*-butyl-**III** and 5,7-di-*tert*-butyl-**III** as well as 5,6-di-*n*-propyl-**III** and 5,8-di-*n*-propyl-**III** have been reported by Chang *et al.* [8]. 6,7-Dichloro- and 5,7,8-trichloro-**III** have been identified among the products of photodegradation of 2,4,5-trichlorophenoxyacetic acdi and 2,4,5-trichlorophenol on titanium oxide [9].

Scheme 2




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **III**, | $R^1$ = | $R^2$ | = $R^3$ | = $R^4$ | = H | | | |
| **IIIa**, | $R^1$ = | $R^3$ | = $R^4$ | = H, | $R^2$ | = Br | | |
| **IIIb**, | $R^1$ = | $R^2$ | = $R^4$ | = H, | $R^3$ | = Br | | |
| **IIIc**, | $R^1$ = | $R^3$ | = $R^4$ | = H, | $R^2$ | = $NO_2$ | | |
| **IIId**, | $R^1$ = | $R^2$ | = $R^4$ | = H, | $R^3$ | = $NO_2$ | | |
| **IIIe**, | $R^1$ = | $R^3$ | = $R^4$ | = H, | $R^2$ | = *t*-Bu | | |
| **IIIf**, | $R^1$ = | $R^2$ | = $R^4$ | = H, | $R^3$ | = *t*-Bu | | |
| **IIIg**, | $R^1$ = | OMe; | $R^2$ | = $R^3$ | = $R^4$ | = H | | |
| **IIIh**, | $R^1$ = | $R^2$ | = $R^3$ | = H, | $R^4$ | = OMe | | |

There are few reports on the preparation of derivatives with substituents in position 3 of the lactone **III**. 3-Aryl and 3-alkyl derivatives, mostly those with the aromatic ring of **III** fully halogenated, have been prepared. The method of synthesis of these compounds involves the reaction of tetraholo-*o*-benzoquinones or other *o*-quinone precursors with ketene derivatives [10] or with mesoionic heterocycles [11]. 3-Aryl derivatives have also been prepared by the reaction of 1-aryl-2-trichloromethylethanols with catechol [12] while 3,3-dimethyl derivatives were obtained in a cyclocondensation of catechol with methyl 2-bromo-2-methyl propionate [13].

Derivatives with alkylidene substituents in position 3 have been reported and those include methylidene [14a,b], ethylidene [14b-d] and benzylidene [14b,e] derivatives. A similar structure has also been postulated for one of the secondary products of treatment of *o*-phenylene thionocarbonate with trialkyl phosphites [14f].

Some of the simple derivatives of **III** appeared in patents and those include 6-bromo-**III (IIIc)** [15], 7-nitro-**III (IIIf)** [16] and 6,8-dinitro-**III** [17], 3-methyl-6-nitro-**III**, 8-methyl-**III** [13] and carbamoyloximes of 3,3-dialkyl-**III** with an additional substituent such as cyano, trifluoromethyl, thiomethyl, methoxyl and nitro in position 7 [18], however, it is difficult to retrieve the incomplete information contained in those patents. Also, the literature data concerning the lactone **III** itself are confusing and inconsistent. In this contribution we would like to report on our study aimed at reexamination of syntheses of lactone **III**, synthesis of some of its simple derivatives as well as provide the high resolution spectral data for these compounds since such data have not been presented. Only $^1$H nmr spectra of **III** (at 60 MHz, [7]) and 6,8-di-*tert*-butyl-**III** and 5,7-di-*tert*-butyl-**III** as well as 5,6-di-*n*-propyl-**III** and 5,8-di-*n*-propyl-**III** (at 100 MHz, [8]) have been reported.

Melting point for lactone **III** has been reported as 57° by Carter and Lawrence [5], 53-55° by Sprecker *et al.* [7] while Ghosh reported 135° [6]. We have repeated all the three procedures confirming that the products of reactions completed according to Sprecker *et al.* and according to Carter and Lawrence are identical and our uncorrected melting point for each of them was 55°. The compound which has been obtained following Ghosh's procedure showed an initial melting point of 133-135° but after two recrystallizations from methanol-water mixture its melting point was 153°. This compound has been identified therefore as (2-hydroxyphenoxy)acetic acid **IIb** for which the melting point of 152° has been reported earlier [5]. Lactone **III** obtained using Ghosh's procedure has been used recently in the synthesis of macrocyclic ligands with amide units [19]. However, it is obvious that the use of either lactone **III** or hydroxyacid **IIb** should lead to the same open-chain amides, which are precursors for macrocycles.

Study of hydroxyacid **IIb** and lactone **III** have revealed that their nmr spectra are similar (see Experimental) and this might be expected for the other pairs hydroxyacid-corresponding lactone. Difficulties were encountered with the observation of both hydroxy protons of **IIa** in $^1$H nmr. Their signals were not observed in methanol-$d_4$ while in less polar acetone-$d_6$ phenolic hydroxy proton appeared as a wide signal while the signal of the carboxylic hydroxy proton was absent. The infrared spectra of **IIb** and **III** have shown a significant difference in the position of carbonyl stretching band which was observed at 1720 cm$^{-1}$ and 1780 cm$^{-1}$, respectively. For the derivatives of **III** however this band was wider and covered most of the region 1770-1730 cm$^{-1}$. The best confirmation of the structure came from the analysis of mass spectra which have shown unequivocally that Ghosh's compound was, in fact, (2-hydroxyphenoxy)acetic acid **IIa**. In the ms spectrum of **IIa** a strong parent ion peak, strong peaks at $(M^+-46)$ and $(M^+-47)$ and a very weak peak of $(M^+-18)$ (which might be the peak of lactone **III** arising from the loss of the water molecule from the parent ion) have been found. The major fragmentation pathway for this compound seems to involve the loss of a carbon dioxide or formic acid molecule. For the lactone **III** a strong parent ion peak has been found with no peaks having a higher molecular mass. The major fragmentation pathway for lactone **III** seems to involve the loss of a carbon monoxide molecule giving rise to the strong peaks $(M^+-28)$ and $(M^+-29)$. For both compounds **IIa** and **III** the next major molecule resulting from the fragmentation of the parent ion is presumably a stable system of 1,3-benzodioxole [20]. A similar fragmentation pattern was observed for the other lactones **IIIa-h**. Thus mass spectrometry is the most reliable method confirming the structure for lactones **III** and corresponding hydroxyacids. It is important to recognize the fact that in solution, particularly in the polar solvents, an equilibrium lactone-hydroxyacid may be established [14b,14d,21,22].

While there is a fair number of reports describing reactions involving a lactone ring opening of **III** [8,11,14b,14d,14e,16,23] only a few literature references describe the reactions of **III** leaving the 1,4-dioxin system intact. A short report describes its reaction with the product of decarboxylation of picolinic acid and yielding 2-(2-hydroxy-2,3-dihydro-1,4-benzodioxin-2(3*H*)-yl)pyridine, although its open-chain counterpart has also been present [21]. Carbamoyloximes of lactone **III** have been synthetized and used as pesticides [18]. Reaction of dimethyl derivatives of **III** with phosphorus pentachloride and hydrofluoric acid converted system **III** into 2,2-difluoro-2,3-dihydro-1,4-benzodioxins patented as insecticides and acaricides [13].

In the course of our work the bromination of lactone **III** under two sets of conditions has been examined. Electrophilic bromination with *N*-bromosuccinimide led to the overall synthesis of two monobrominated isomers **IIIa** and **IIIb** with the latter being the major product. Both of these isomers have been isolated and characterized. Photobromination of **III** with *N*-bromosuccinimide led to the same two isomers with **IIIa** being the major product isolated from this reaction. The presence of **IIIb** was confirmed by analysis of the $^1$H nmr spectrum of the crude lactonization reaction product which was shown to be a mixture of two isomers. The structure of these isomers has been proposed on the basis of the spectroscopic data and mechanistic considerations. The analysis of the nmr spec-

tra for both isomers proves that bromination did occur in the aromatic ring. The splitting patterns observed in the aromatic region of proton spectra are similar for both isomers and consistent with what may be expected for a trisubstituted benzene ring. Analysis of $^{13}C$ nmr spectra of **IIIa** and **IIIb** shows their similarity to the spectrum of **III** itself with a distinct change in the chemical shift for the signals of the quaternary aromatic carbon atoms that carry a bromine substituent. While the data show that there are indeed two isomers formed it cannot be unequivocally determined exactly which isomer has been isoated from each reaction due to the similarity of the analytical data for both isomers. It is also difficult to explain why there would be a different major product from electrophilic and photolytic bromination since both these methods would be expected to give the same isomer as the major product. It may be noted that electrophilic chlorination and bromination of guaiacol give 5-chloro- and 5-bromo-2-methoxyphenol as the only monohalo derivatives, respectively [24]. We expect then that under the electrophilic conditions the incoming bromine should be found in position 7 of the system for the major isomer **IIIb** and in position 6 for the other isomer **IIIa**, which is a major product of the photolytic reaction.

The use of substituted catechols in the lactone synthesis should lead to the formation of two isomeric lactones if the starting catechol is not symmetrical. We have examined such reactions using available catechols. The use of 4-nitrocatechol resulted in the formation of two isomeric nitro derivatives, **IIIc** and **IIId**. The major product of this reaction, **IIId**, has been isolated and fully characterized. Despite many attempts isomer **IIIc** has not been isolated although its spectral data was deduced from the spectra of the mixture of two isomers. The nmr spectra show only minor but distinct differences in the chemical shifts for signals both in proton and carbon spectra but it can be clearly seen that those are indeed two isomers. It should be noted that the presence of the nitro group would deactivate the aromatic ring toward further electrophilic substitution. This was confirmed in an attempted bromination of the isomeric mixture of **IIIc** and **IIId** under mild conditions with NBS. The reaction resulted in recovery of over 90% of the starting material with no traces of brominated product. The use of 4-*tert*-butylcatechol and 3-methoxycatechol in similar reactions led to the formation and isolation of single isomers of lactones **IIIe** and **IIIh**, respectively. Unlike in the case of the nitrolactones **IIIc** and **IIId** we were unable to confirm unambiguously that the two other respective isomers, **IIIf** and **IIIg**, were formed in the reactions. Structures of the isomers that we have isolated have been elucidated on the basis of analytical data presented in the Experimental part and mechanistic considerations.

It is interesting to note that in some of the described reactions a different degree of selectivity was observed. Using a stepwise approach and in one case a protective group, Chang *et al.* were able to synthesize selectively both 6,8-di-*tert*-butyl-1,4-benzodioxin-2(3*H*)-one and 5,7-di-*tert*-butylbenzodioxin-2(3*H*)-one from 3,5-di-*tert*-butylcatechol although their approach was less successful in the case of di-*n*-propylcatechols [8]. The regioselectivity observed in each case was explained as a result of the steric effect of 3-*tert*-butyl group which hinders the access to the 2-hydroxy group leaving the 1-hydroxy group open for the first reaction of the lactone synthesis sequence. The controlled sequence of lactone formation proposed by these authors shows that the steric effects of the substituent present in the proximity of the hydroxy group will hinder the reaction of this hydroxy group with an electrophile. This should lead to formation of only one isomer of hydroxyphenoxyacid and further to one isomer of lactone. Another possible factor influencing the outcome of these reactions could be electronic effects. Due to the presence of substituents in the aromatic ring one hydroxy group should be more acidic than the other which will lead to the predominant formation of one isomer of hydroxyphenoxyacid in the first step. Using these assumptions the major isomer that should have been obtained from 4-nitrocatechol is the 7-nitro isomer **IIId** since the hydroxy group *para* to the nitro should be more acidic as a result of the electron withdrawing effects of the nitro group in the absence of steric effects. It is at this position that the formation of the intermediate hydroxyphenoxyacid should be favored and this should lead ultimately to the formation of **IIId** as the major product of the sequence. In the case of 4-*tert*-butylcatechol no steric hindrance may be exerted again by the substituent so the electronic effects should be responsible for the formation of 6-*tert*-butyl-1,4-benzodioxin-2(3*H*)-one **IIIe** as the major product. The effect of the *tert*-butyl substituent is electron donating, therefore perferential formation of the positional isomer other than in the case of nitro group should be expected. For 3-methoxycatechol both electronic and steric effects should favor the initial formation of 2-hydroxy-3-methoxyhydroxyacid and, in the end of the sequence, of 8-methoxybenzodioxin-1,4-2(3*H*)-one **IIIh**. The study of the influence of both steric and electronic factors on the selectivity of the first step *i.e.* formation of hydroxyphenoxyacid and later on of lactone, is currently under way.

## EXPERIMENTAL

Melting points are uncorrected. All the chemicals used were of reagent grade quality and were purified according to the standard procedures. The 250 MHz $^1H$ and 62.5 MHz $^{13}C$ nmr spectra were recorded on a Bruker AC250F spectrometer at the Atlantic Regional Magnetic Resonance Centre, Halifax; chemical

shifts ($\delta$) are reported in ppm downfield from TMS (internal for proton, calculated from the solvent shift for carbon-13 spectra). The ir spectra have been recorded with a Perkin Elmer 299 instrument using nujol mulls (with te exception of compound **IIIh** for which chloroform solution was used) and the stretching C=O frequency region is reported. Mass spectra were obtained using electron impact ionization at 70 eV; compounds **IIIa** and **IIIb** show a pattern typical for the bromo derivatives due to the presence of isotopic peaks. All the lactone synthesis experiments were completed starting with 0.01 mole of catechols with the exception of lactone **III**, which has been synthetized on 0.1 mole scale. All the lactones are unstable and decompose upon storage.

General Procedure for the Synthesis of Lactones **III** (Modified Ghosh's Procedure).

The synthesis of **III** described by Ghosh [6] was used with modifications and an additional step including lactone ring closure according to Chang *et al.* [8]. Sodium, 2.3 g (0.1 mole) was dissolved in 100 ml of absolute ethanol. Catechol, 11.0 g (0.1 mole), was then added followed by slow, dropwise addition of 18.37 g (12.2 ml, 0.11 mole) of ethyl bromoacetate. The mixture was refluxed for 16 hours then the solvent was evaporated, the inorganic salts filtered off and washed with acetone. After removal of acetone the brown oil that remained was distilled under vacuum to yield a clear, viscous oil. The oil was quenched with 20 ml of concentrated hydrochloric acid and refluxed for one hour. Upon cooling a white solid of (2-hydroxyphenoxy) acetic acid separated from solution. This product was collected and dissolved in 200 ml of benzene and refluxed, using a Dean-Stark stillhead, with a catalytic amount of PTSA or boron trifluoride-methanol complex for 3 hours. After cooling the solvent was evaporated giving a yellow-white solid, the lactone **III**, which was collected and recrystallized from toluene. Alternatively, the lactone **III** was recovered by chromatography on a silica gel column (15 cm x 2 cm) using chloroform to elute the lactone.

Vacuum distillation of **IIa** or **IIb** [5] gave lactone **III** in 18% and 20% yield, respectively.

General Procedure for Direct Synthesis of Lactones **III**.

A procedure of Sprecker *et al.* [7] with slight modifications has been applied. To a solution of catechol (11.0 g, 0.1 mole) in 100 ml of toluene, 10.2 g (14.1 ml, 0.2 mole) of anhydrous triethylamine was added at 50°. Chloroacetyl chloride (11.3 g, 8.0 ml, 0.1 mole) in 25 ml of toluene was added dropwise and the mixture was refluxed for 3 hours. The reaction mixture was cooled then, the solid which precipitated was filtered out and the clear filtrate evaporated to dryness. The remaining solid was chromatographed as above yielding pure lactone.

(2-Hydroxyphenoxy)acetic Acid **IIb**.

Following original work by Ghosh with two recrystallizations of the product from 1:1 methanol-water this compound was isolated as white-pink needles, yield 3.53 g (21%), mp 153° (lit 152° [5]); ir: $\nu$ CO 1720 $cm^{-1}$; $^1H$ nmr (acetone-$d_6$): $\delta$ 4.61 (s, 2H, $CH_2$), 6.22-6.65 (broad s, phenolic OH), 6.72-6.89 (2m, 4H, aromatic); $^{13}C$ nmr (acetone-$d_6$): $\delta$ 66.9 ($CH_2$), 114.8, 117.1, 120.8, 123.7, 147.0 (quaternary), 147.8 (quaternary), 173.6 ($C$=O) (nmr spectra in methanol-$d_4$ are nearly identical); ms: m/z 168 ($M^+$), 150, 122, 121 (100), 109, 95, 81.

*Anal.* Calcd. for $C_8H_8O_4$: C, 57.14; H, 4.80. Found: C, 56.95; H, 4.81.

1,4-Benzodioxin-2(3*H*)-one **III**.

Lactone **III** was obtained as a yellow-white solid, yield 2.7 g (18%), mp 55° (lit 53-55° [7], 57° [5]); ir: $\nu$ CO 1780 $cm^{-1}$; $^1H$ nmr (acetone-$d_6$): $\delta$ 4.71 (s, 2H, $CH_2$), 6.63-6.88 (m, 1H, aromatic), 6.90-6.98 (m, 2H, aromatic), 7.06-7.12 (m, 1H, aromatic); $^{13}C$ nmr (acetone-$d_6$): $\delta$ 67.8 ($CH_2$), 117.0, 116.3, 120.5, 123.9, 147.3 (quaternary), 148.6, (quaternary), 172.1 ($C$=O) (nmr spectra in methanol-$d_4$ are nearly identical); ms: m/z 150 ($M^+$), 122, 121 (100), 80, 63.

*Anal.* Calcd. for $C_8H_6O_3$: C, 64.00; H, 4.03. Found: C, 63.85; H, 3.86.

6- and 7-Bromo-1,4-benzodioxin-2(3*H*)-one **IIIa** and **IIIb**.

To a solution of 1.5 g (0.01 mole) of **III** in 25 ml of anhydrous tetrahydrofuran, 2.14 g (0.012 mole) of *N*-bromosuccinimide in 40 ml of tetrahydrofuran was added dropwise *via* a dropping funnel, resulting in a dark orange color. The solution was refluxed for 1/2 hour after which it became light yellow. The solvent was evaporated to give a yellow oil. Succinimide was removed by crystallization of oil from chloroform while the remaining products were purified by passing the sample through a silica gel column. Acetone and methanol fractions were combined and the nmr spectra of the mixture examined. These spectra revealed that a mixture of two monobrominated isomeric compounds was obtained. Separation of these isomers was done by repeatedly extracting the solid into a mixture of hexane/acetone 1:1 and collecting the insoluble product. The insoluble compound proved to be the major product of bromination while from the extracts the second isomer was obtained upon crystallization. The isomeric products were treated with benzene/PTSA and chromatographed as above. The overall yield of the reaction was 0.62 g (27%).

6-Bromo-1,4-benzodioxin-2(3*H*)-one **IIIa**.

Isomer **IIIa** was separated as a white powder, yield 0.09 g (4%), mp 111-113°; ir: 1760 $cm^{-1}$; $^1H$ nmr (acetone-$d_6$): $\delta$ 4.69 (s, 2H, $CH_2$), 6.73 (d 8.4, 1H, aromatic), 6.96 (d 8.4, d 2.1, 1H, aromatic), 7.01 (d 2.1, 1H, aromatic); $^{13}C$ nmr (methanol-$d_4$) $\delta$ 67.0 ($CH_2$), 111.5, 117.8, 118.3, 126.1 (quaternary), 147.3 (quaternary), 147.7 (quaternary), 173.1 ($C$=O) (nmr spectra in methanol-$d_4$ are identical); ms: m/z: 230 ($M^+$), 228, 202, 200 (100), 189, 187, 161, 159, 122, 121, 94, 79.

*Anal.* Calcd. for $C_8H_5BrO_3$: C, 41.95; H, 2.20. Found: C, 42.03; H, 2.01.

7-Bromo-1,4-benzodioxin-2(3*H*)-one **IIIb**.

This isomer was obtained as a white powder, yield 0.30 g (13%), mp 123-125°; ir: $\nu$ CO 1768 $cm^{-1}$; $^1H$ nmr (acetone-$d_6$): $\delta$ 4.80 (s, 2H, $CH_2$), 6.83 (d, 8.5 Hz, 1H, aromatic), 7.04 (d 8.5, d 2.1, 1H, aromatic), 7.16 (d 2.1, 1H, aromatic); $^{13}C$ nmr (acetone-$d_6$): $\delta$ 67.7 ($CH_2$), 111.0, 118.4, 119.4, 126.4 (quaternary), 147.9 (quaternary), 147.7 (quaternary), 171.2, ($C$=O) (nmr spectra in methanol-$d_4$ are identical); ms: m/z 230 ($M^+$), 228, 202, 200, 180, 152 (100), 137, 122, 121, 107, 95.

*Anal.* Calcd. for $C_8H_5BrO_3$: C, 41.95; H, 2.20. Found: C, 41.82; H, 2.28.

Photolytic Preparation of **IIIa** and **IIIb**.

The mixture of 1.5 g (0.01 mole) of **III**, 2.14 g, (0.012 mole) of *N*-bromosuccinimide and a trace of benzoyl peroxide were dis-

solved in 200 ml anhydrous tetrahydrofuran and irradiated, without heating, in a photochemical reactor (300 nm) for 3 hours. The solvent was removed yielding a crude black solid, which was extracted with hot chloroform. The remaining grey solid was taken with acetone; both solutions were combined and worked out as previously. However, the isomer **IIIa** was the major product this time. The overall yield of the reaction was 0.48 g (21%); the yield of the recovered isomer **IIIa** was 11%. Similar experiments with isomeric mixtures of nitro-**III** have been conducted resulting in no bromination of the substrate.

6- and 7-Nitro-1,4-benzodioxin-2(3*H*)-one **IIIc** and **IIId**.

Starting from 4-nitrocatechol 0.92 g (47%) of the mixture of products **IIIc** and **IIId** was obtained using a modified Ghosh's procedure. Using a procedure of Sprecker *et al.* similar mixture was obtained in 19% yield.

7-Nitro-1,4-benzodioxin-2(3*H*)-one **IIId**.

This isomer was separated as yellow-brown crystals from toluene, yield 0.51 g (26%), mp 159° (lit 157° [16]); ir: $\nu$: CO 1762 $cm^{-1}$; $^1H$ nmr (methanol-$d_4$): $\delta$ 4.89 (s, 2H, $CH_2$), 7.05 (d 9.0, 1H, aromatic), 7.78 (d 2.4, 1H, aromatic), 7.87 (d 8.8, d 2.5, 1H, aromatic); $^{13}C$ nmr (methanol-$d_4$): $\delta$ 67.3 ($CH_2$), 111.1, 114.1, 119.5, 143.1 (quaternary), 148.8 (quaternary), 154.8 (quaternary), 172.0 ($C$=O); ms: m/z 195 ($M^+$), 167, 137, 122, 121, 107, 91, 65 (100).

*Anal.* Calcd. for $C_8H_5NO_5$: C, 49.24; H, 2.58; N, 7.18. Found: C, 49.56; H, 2.28; N, 7.03.

The minor product, 6-nitro-1,4-benzodioxin-2(3*H*)-one **IIIc**, has not been isolated although its nmr spectral data was determined from the spectra of the mixture; $^1H$ nmr (methanol-$d_4$): $\delta$ 4.84 (s, 2H, $CH_2$), 6.97 (d 9.0, 1H, aromatic), 7.62 (d 2.7, 1H, aromatic), 7.69 (d 8.8, d 2.7, 1H, aromtic); $^{13}C$ nmr (methanol-$d_4$): $\delta$ 66.5 ($CH_2$), 111.5, 116.7, 120.2, 146.8 (quaternary), 148.1 (quaternary); 153.2 (quaternary), 170.6 ($C$=O).

6- and 7-*tert*-Butyl-1,4-benzodioxin-2(3*H*)-one **IIIe** and **IIIf**.

Starting from 4-*tert*-butylcatechol, 0.95 g (46%) of the mixture of products **IIIe** and **IIIf** was obtained using a modified Ghosh's procedure. Using a procedure of Sprecker *et al.* a similar mixture was obtained in 11% yield.

6-*tert*-Butyl-1,4-benzodioxin-2(3*H*)-one **IIIe**.

Isomer **IIIe** was separated upon the crystallization from dichloromethane as a beige powder, yield 0.72 g (35%), mp 129-130°; ir: $\nu$ CO 1750 $cm^{-1}$; $^1H$ nmr (methanol-$d_4$): $\delta$ 1.30 (s, 9H, $CH_3$), 4.96 (s, 1H, $CH_2$), 6.88 (d 8.4, 1H, aromatic), 6.98 (d 8.4, d 2.2, 1H, aromatic), 7.02 (d 2.2, 1H aromatic); $^{13}C$ nmr (methanol-$d_4$): $\delta$ 31.8 ($CH_3$), 35.2 [$C(CH_3)_3$], 67.7, ($CH_2$), 115.0, 116.2, 120.3, 146.9 (quaternary), 147.9 (quaternary), 148.8 (quaternary), 173.0 ($C$=O); ms: m/z 206 ($M^+$), 191 (100), 163, 135, 122, 121, 105, 91.

*Anal.* Calcd. for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 70.24; H, 6.96.

The nmr spectra of the mother liquor revealed the presence of two other compounds, which are probably a structural isomer and possibly an open-chain compound. The amounts of these two products were too small for their isolation and unambiguous identification.

5- and 8-Methoxybenzodioxin-1,4-2(3*H*)-one **IIIg** and **IIIh**.

Starting from 3-methoxycatechol 0.49 g (27%) of the mixture containing mostly isomer **IIIh** and some other unidentified products was obtained using a modified Ghosh's procedure. Using a procedure of Sprecker *et al.* similar mixture was obtained in 9% yield. The nmr spectra of the crude product has shown the presence of only one isomer with minor impurities.

8-Methoxybenzodioxin-1,4-2(3*H*)-one **IIIh**.

This compound separated as a brown oil from benzene or chloroform, yield 0.40 g (22%); ir: $\nu$ CO 1755 $cm^{-1}$; $^1H$ nmr (methanol-$d_4$): $\delta$ 3.83 (s, 3H, O-$CH_3$), 4.70 (s, 2H, $CH_2$), 6.57 (d 8.4, d 1.2, 1H, aromatic), 6.70 (d 8.4, d 1.2, 1H, aromatic), 7.00 (t 8.4, 1H aromatic); $^{13}C$ nmr (methanol-$d_4$): $\delta$ 56.7 (O-$CH_3$), 67.0 ($CH_2$), 107.5, 108.2, 125.4, 138.1 (quaternary), 152.8 (quaternary), 154.7 (quaternary), 173.3 ($C$=O); ms: m/z 180 ($M^+$), 151, 139 (100), 122, 121, 107, 95.

*Anal.* Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 59.97; H, 4.96.

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