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The cleavage reaction of some 1,3-benzodioxole derivatives with magnesium bromide and acetic anhydride has been studied. The reactions have been carried out in acetonitrile solution at room temperature. In all of the 1,3-benzodioxoles studied, the opening of the heterocyclic ring with formation of bromides, alkenes and their corresponding products of hydrolysis have been observed. The competitive electrophilic substitution on the benzene ring was very limited and was insignificant when a large excess of the cleavage reagent was used. The structures of newly prepared compounds have been determined by elemental analysis, spectroscopic data and comparison with authentic samples.

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Recently the cleavage of the ether bond of some alkoxy and 1,3-benzodioxoles by Grignard reagents (1) and aluminum and magnesium bromide (2) has been studied; it has been noted that reactions were reproducible and proceeded according to the rules of orientation.

In order to control the cleavage reaction of the C—O bond in the benzodioxole system and to ascertain whether or not it could occur under milder conditions and in order to avoid the tedious de-solvating procedures generally required using Grignard reagents, we undertook a study on the reaction of some 1,3-benzodioxoles with magnesium bromide and acetic anhydride.

The ability of acid anhydrides and acyl chlorides to cleave ethers has been known for several years (3). It has also been observed that acyl chlorides are much more effective than the corresponding anhydrides and the addition of Lewis acids makes the reaction much easier (4). On the other hand it has been reported that magnesium salts are not particularly active as catalytic agents in the cleavage of the ether bond (2,5).

However, surprisingly, when the reactions were carried out with acetic anhydride and magnesium bromide, the cleavage of one or both of the ether bonds was observed. Working in this way, some carbinols and 2-bromoalkoxyphenylacetates, although quite difficult to obtain by an alternative method could also be prepared.

The cleavage reactions of the 1,3-benzodioxoles have been carried out at room temperature with an equimolar amount of magnesium bromide, prepared *in situ*, and with two equivalents of acetic anhydride in acetonitrile.

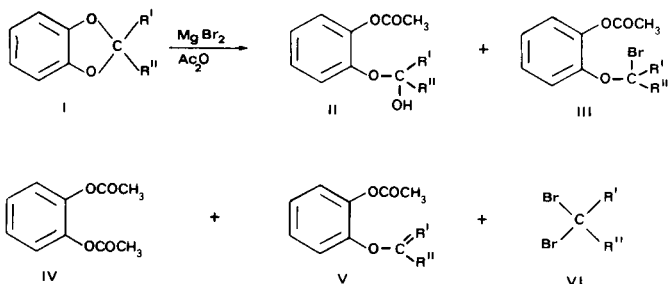
The products obtained are summarized in Scheme 1. The new derivatives II, III and V are thermally stable and can be distilled under reduced pressure, however, they all spontaneously hydrolyse in the presence of moisture.

The structure of all the compounds has been determined by elemental analysis and spectroscopic data or comparison with authentic samples (Scheme 1).

During the reaction a small amount of the 5-acetyl derivative X was also formed. It became insignificant when a large excess of the cleavage reagent was used, but it was the main reaction product when aluminum halides were used instead of magnesium bromide. The amount of compound X which was generated in the cleavage reaction also depended on the nature of the substrate. In fact while the amount was minimal for the 1,3-benzodioxole Ia it increased with the increase of the steric congestion about the C<sub>2</sub>, and in the case of 2-methyl-2-isopropyl-1,3-benzodioxole (Ig) it was about 12%.

Very likely, the oxonium salt formed as a first step which deactivated the benzene ring increasing the cleavage reaction of the ether bond while the formation of the intermediate oxonium in the benzodioxoles with sterically demanding groups on the C<sub>2</sub>, was hindered, thus a competitive acylation reaction on the aromatic ring was favoured (3a,b,c). Subsequently the reactant could attack the second ethereal oxygen (Scheme 2).

Scheme 1



a) R<sup>I</sup> = R<sup>II</sup> = H

b) R<sup>I</sup> = R<sup>II</sup> = CH<sub>3</sub>

c) R<sup>I</sup> = C<sub>2</sub>H<sub>5</sub>, R<sup>II</sup> = n-C<sub>4</sub>H<sub>9</sub>

d) R<sup>I</sup> = CH<sub>3</sub>, R<sup>II</sup> = n-C<sub>4</sub>H<sub>9</sub>

e) R<sup>I</sup> R<sup>II</sup> = (CH<sub>2</sub>)<sub>4</sub>

f) R<sup>I</sup> R<sup>II</sup> = (CH<sub>2</sub>)<sub>5</sub>

g) R<sup>I</sup> = CH<sub>3</sub>, R<sup>II</sup> = i-C<sub>3</sub>H<sub>7</sub>

Scheme 2

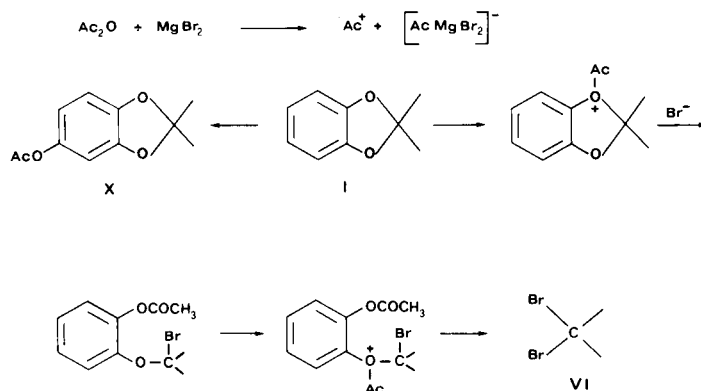


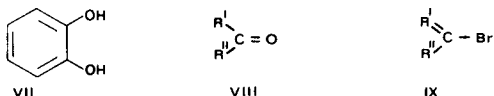
Table 1

Action of Magnesium Bromide-Acetic Anhydride on the 1,3-Benzodioxoles for 15 Hours at Room Temperature

Starting material	% Cleavage	% Products			
		II	III	V	X
1,3-Benzodioxole (Ia)	92	—	70	—	Trace
2,2-Dimethyl-1,3-benzodioxole (Ib)	90	30	34	8	Trace
2-Ethyl-2- <i>n</i> -butyl-1,3-benzodioxole (Ic)	86	22	42	12	8
2-Methyl-2- <i>n</i> -propyl-1,3-benzodioxole (Id)	85	15	37	20	8
Spiro[1,3-benzodioxole-2,1'-cyclopentane] (Ie)	88	37	18	21	4
Spiro[1,3-benzodioxole-2,1'-cyclohexane] (If)	85	32	20	16	5
2-Methyl-2-isopropyl-1,3-benzodioxole (Ig)	65	13	16	27	12

Yields refer to the products obtained after washing and neutralization.

The glc analyses of the reaction mixture, after hydrolysis, showed the presence of products VII, VIII and IX as determined by comparison with reference to authentic samples.



The formation of compound II occurred in a second step, probably as the result of the nucleophilic attack on compound III of the base used for the neutralization. This was confirmed by the observation that the carbinol amount became significant only after neutralization of the reaction mixture; at the same time, the per cent of compound III decreased and when III was kept for some time in the presence of an aqueous sodium carbonate solution, it gave, in part, only the corresponding carbinol derivative II. In the cleavage reaction of 1,3-benzodioxole Ia, formation of the carbinolic compound did not occur. Very little of the *gem*-dibromide was obtained with the procedure and then only by working with a large excess of the reactant and, at reflux temperature, the dibromide became the main product of the cleavage reaction.

## EXPERIMENTAL

Boiling points were uncorrected and obtained from distillation or with a boiling point apparatus. Infrared spectra were recorded on a Perkin Elmer Model 157 G spectrophotometer. Absorption frequencies are quoted in reciprocal centimeters; samples were examined as potassium bromide pellets or as thin-film. The nmr spectra were determined on a Varian FT-80A spectrometer; chemical shifts were measured in ppm ( $\delta$ ) using tetramethylsilane as the internal reference. Exchangeable protons were detected by deuterium oxide addition. The glc analyses were performed on a Carlo Erba GV instrument equipped with SE-30 column (2 m  $\times$  0.5 cm, 5% chromosorb W 60/80). The hplc analyses were performed using a Perkin Elmer 601 liquid chromatograph. A Merck RP 18 column was used (250  $\times$  4 mm id, flow rate: 1 ml minute<sup>-1</sup>; mobile phase 50:50 methanol-water, detector UV/visible Perkin-Elmer LC 55,  $\lambda = 254$  nm). Microanalyses for CHN were carried out on a Carlo Erba model 1106 Elemental-Analyzer. Analyses for bromine were performed according to literature procedures (6).

### Starting Materials.

1,3-Benzodioxole (7), 2,2-dimethyl-1,3-benzodioxole (8), 2-ethyl-2-(*n*-butyl)-1,3-benzodioxole (9), 2-methyl-2-(*n*-propyl)-1,3-benzodioxole (8), 2-methyl-2-isopropyl-1,3-benzodioxole (10), spiro[1,3-benzodioxole-2,1'-cyclopentane] (8), spiro[1,3-benzodioxole-2,1'-cyclohexane] (8) were prepared according to established procedures.

All the 2,2-disubstituted-1,3-benzodioxole derivatives could also be prepared, in good yields, by distilling azeotropically equimolar amounts of catechol and ketone in the presence of traces of *p*-toluenesulphonic acid, while 1,3-benzodioxole could be prepared by treatment of the

catechol with dibromomethane in the presence of a phase transfer catalyst as it has been described for the synthesis of 1,3-benzoxathiole (11).

#### Authentic Samples.

Catechol, acetone, dibromomethane, 3-heptanone, 2-pentanone, cyclopentanone, cyclohexanone, 3-methyl-2-butanone, 2-bromopropene, 2,2-dibromopropane, as well as all the solvents, were commercial products and have been used without further purification; 2-bromo-3-methyl-2-butene (12), 1-bromo-1-cyclopentene (13), 1-bromo-1-cyclohexene (13), 2-bromo-2-pentene (14), 2,2-dibromopentane (15), 3,3-dibromo-2-methylbutane (16), 1,1-dibromocyclopentane (17) and 1,1-dibromocyclohexane (17) were prepared according to literature procedures. Compounds VIc and IXc were prepared by the following method.

#### 3,3-Dibromoheptane (VIc) and 3-Bromo-3-heptene (IXc).

To a stirred solution of 3-heptanone (5.7 g, 50 mmoles) in 50 ml of dry diethyl ether, Phosphorus tribromide (13.5 g, 50 mmoles) and bromine (8 g, 50 mmoles) were added dropwise. The solution was stirred at room temperature for 24 hours and then washed with water. The ether layer was dried over anhydrous magnesium sulfate and the solvent evaporated. The residue, after distillation under reduced pressure, gave VIc and IXc.

#### 3,3-Dibromoheptane (VIc).

This compound was obtained in a yield of 51% (1.3 g), bp 188° (760 mm);  $n_D^{25}$  1.4650; nmr (deuteriochloroform):  $\delta$  4.43-4.10 (m, 4 H, 2  $\text{CH}_2\text{—CH}_2$ ), 2.83-2.36 (m, 4 H,  $\text{—CH}_2\text{CH}_2\text{—}$ ), 1.83-1.66 (t, 3 H,  $\text{CH}_3\text{—CH}_2\text{—C}$ ) and 1.17-0.96 ppm (m, 3 H,  $\text{CH}_3\text{—CH}_2\text{—CH}_2$ ).

*Anal.* Calcd. for  $\text{C}_7\text{H}_{14}\text{Br}_2$ : C, 32.55; H, 5.42; Br, 62.01. Found: C, 32.63; H, 5.44; Br, 61.92.

#### 3-Bromo-3-heptene (IXc).

This compound was obtained in a yield of 34% (0.6 g), bp 203° (760 mm);  $n_D^{25}$  1.4732; nmr (deuteriochloroform):  $\delta$  4.93-4.66 (m, 1 H,  $\text{=CH—CH}_2$ ), 4.43-4.10 (m, 4 H, 2  $\text{CH}_2\text{—CH}_2$ ), 2.83-2.50 (m, 2 H,  $\text{CH—CH}_2\text{—CH}_2$ ), 1.83-1.66 (t, 3 H,  $\text{CH}_3\text{—CH}_2\text{—C}$ ) and 1.08-0.90 ppm (m, 3 H,  $\text{CH}_3\text{—CH}_2\text{—CH}_2$ ).

*Anal.* Calcd. for  $\text{C}_7\text{H}_{13}\text{Br}$ : C, 47.45; H, 7.34; Br, 45.19. Found: C, 47.54; H, 7.36; Br, 45.09.

#### General Procedure for the Cleavage of 1,3-Benzodioxoles.

1,2-Dibromoheptane (9.39 g, 50 mmoles) was added dropwise with stirring under nitrogen to magnesium turnings (1.21 g, 50 mmoles) and dry diethyl ether (50 ml). When all the magnesium had disappeared, the ether was distilled under reduced pressure and replaced with dry acetonitrile (50 ml). To its stirred suspension, cooled in an ice-water bath, dry 1,3-benzodioxole derivative (50 mmoles) and acetic anhydride (10.2 g, 100 mmoles) were added. The reaction was kept at room temperature and stirred for an additional 15 hours, then neutralized with a saturated sodium bicarbonate solution and extracted with diethyl ether.

The ethereal solution was dried over anhydrous magnesium sulfate and evaporated. The dark brown oily residue was distilled under reduced pressure or chromatographed by column on silica gel.

#### Cleavage of 1,3-Benzodioxole (Ia).

Cleavage of Ia (6.1 g, 50 mmoles) under the previously described conditions gave, after distillation, 8.6 g (70% yield) of 2-bromomethoxyphenylacetate (IIIa), bp 115° (760 mm); ir (film): 1740 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.74 (s, 4 H aromatic), 4.05 (s, 2 H,  $\text{—O—CH}_2\text{—Br}$ ) and 2.09 ppm (s, 3 H,  $\text{O—CO—CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_9\text{H}_9\text{BrO}_3$ : C, 44.10; H, 3.70; Br, 32.65. Found: C, 43.99; H, 3.69; Br, 32.65.

#### Cleavage of 2,2-Dimethyl-1,3-benzodioxole (Ib).

Cleavage of Ib (7.5 g, 50 mmoles), under the previously described conditions, gave after distillation a mixture of 2-( $\alpha$ -hydroxyisopropoxy)-1-acetoxybenzene (IIb), 2-( $\alpha$ -bromoisopropoxy)-1-acetoxybenzene (IIIb) and 2-(isopropoxy)-1-acetoxybenzene (Vb). The glc analysis of the mixture

showed the ratio of II to III and V to be 3:3.4:0.8. A mixture fraction, after hydrolysis, analyzed by glc, also showed the presence of catechol, 2,2-dibromopropane (VIa), 2-bromopropene (IXa) and acetone (VIIIa).

#### 2-( $\alpha$ -Hydroxyisopropoxy)-1-acetoxybenzene (IIb).

This compound was obtained in a yield of 30% (3.15 g), bp 70-71° (5 mm);  $n_D^{25}$  1.4928; ir (film): 3360 (OH), 1730 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.68 (s, 4 H aromatic), 2.06 (s, 3 H,  $\text{—O—CO—CH}_3$ ), 1.98 (s, 1 H, OH deuterium oxide exchanged) and 1.59 ppm (d, 6 H, 2  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_4$ : C, 62.84; H, 6.71. Found: C, 62.71; H, 6.75.

#### 2-( $\alpha$ -Bromoisopropoxy)-1-acetoxybenzene (IIIb).

This compound was obtained in a yield of 34% (4.63 g), bp 135° (10 mm);  $n_D^{25}$  1.5190; ir (film): 1740 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.68 (s, 4 H aromatic), 2.04 (s, 3 H,  $\text{O—CO—CH}_3$ ) and 1.59 ppm (s, 6 H, 2  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{Br}$ : C, 48.35; H, 4.79; Br, 29.28. Found: C, 48.47; H, 4.81; Br, 29.21.

#### 2-(Isopropoxy)-1-acetoxybenzene (Vb).

This compound was obtained in a yield of 8% (0.76 g), bp 120-121° (5 mm); ir (film): 1740 (C=O), 1235 (C—O), 940  $\text{cm}^{-1}$  (C=C); nmr (deuteriochloroform):  $\delta$  6.81 (s, 4 H aromatic), 6.10 (s, 2 H,  $\text{=CH}_2$ ), 2.09 (s, 3 H,  $\text{O—CO—CH}_3$ ) and 1.64 ppm (s, 3 H,  $\text{=C—CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{12}\text{O}_3$ : C, 68.73; H, 6.29. Found: C, 68.56; H, 6.29.

#### Cleavage of 2-Ethyl-2-(*n*-butyl)-1,3-benzodioxole (Ic).

Cleavage of Ic (10.31 g, 50 mmoles) under the previously described conditions, gave after distillation a mixture of 2-( $\alpha$ -hydroxy- $\alpha$ -ethylamlyoxy)-1-acetoxybenzene (IIc), 2-( $\alpha$ -bromo- $\alpha$ -ethylamlyoxy)-1-acetoxybenzene (IIIc) and a mixture of alkenes Vc. The glc analysis of the mixture showed the ratio of II to III and V to be 1.1:2.1:0.6. A mixture fraction, after hydrolysis, analyzed by glc and hplc also showed the presence of catechol (VII), 3,3-dibromoheptane (VIc), 3-heptanone (VIIIc), 3-bromo-2-heptene (IXc) and 2-ethyl-2-*n*-butyl-5-acetyl-1,3-benzodioxole (Xc).

#### 2-( $\alpha$ -Hydroxy- $\alpha$ -ethylamlyoxy)-1-acetoxybenzene (IIc).

This compound was obtained in a yield of 22% (2.9 g), bp 85° (5 mm); ir (film): 3320 (OH), 1740 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.82 (s, 4 H aromatic), 2.23-1.95 (m, 2 H,  $\text{—CH}_2\text{—CH}_3$ ), 1.81-1.68 (m, 2 H,  $\text{—CH}_2\text{—(CH}_2)_2\text{—CH}_3$ ), 2.10 (s, 1 H, OH deuterium oxide exchanged), 2.00 (s, 3 H,  $\text{O—CO—CH}_3$ ), 1.43-1.26 (m, 4 H,  $\text{—CH}_2\text{—CH}_2\text{CH}_2\text{CH}_3$ ) and 1.06-0.81 ppm (t + m, 6 H, 2  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{22}\text{O}_4$ : C, 67.64; H, 8.33. Found: C, 67.50; H, 8.28.

#### 2-( $\alpha$ -Bromo- $\alpha$ -ethylamlyoxy)-1-acetoxybenzene (IIIc).

This compound was obtained in a yield of 42% (6.9 g), bp 120° (5 mm);  $n_D^{25}$  1.4729; ir (film): 1730 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.74 (s, 4 H aromatic), 1.98 (s, 3 H,  $\text{O—CO—CH}_3$ ), 2.24-1.95 (m, 2 H,  $\text{—CH}_2\text{—CH}_3$ ), 1.86-1.78 (m, 2 H,  $\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{CH}_3$ ), 1.41-1.27 (m, 4 H,  $\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$ ) and 1.10-0.91 (t + m, 6 H, 2  $\text{CH}_3$ ).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{21}\text{O}_3\text{Br}$ : C, 54.71; H, 6.38; Br, 24.31. Found: C, 54.78; H, 6.40; Br, 24.19.

A mixture of the alkenes 2-(1-ethyl-1-amlyenoxy)-1-acetoxybenzene and 2-(1-ethylidenamlyoxy)-1-acetoxybenzene (Vc), (2 g, 12% yield), bp 133-135° (10 mm) was obtained.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{20}\text{O}_3$ : C, 72.58; H, 8.06. Found: C, 72.51; H, 8.08.

The chromatographic analysis showed that the product consisted of a mixture of the two possible isomers in the ratio of 95:5. The ir and nmr data agreed with the structure Vc. Likely, the predominant alkene is the most stable, that is with the double bond in the butyl chain.

#### Cleavage of 2-Methyl-2-(*n*-propyl)-1,3-benzodioxole (Id).

Cleavage of Id (8.9 g, 50 mmoles), under the previously described conditions, gave after distillation 2-( $\alpha$ -hydroxy- $\alpha$ -methylbutoxy)-1-acetoxybenzene (IIId), 2-( $\alpha$ -bromo- $\alpha$ -methylbutoxy)-1-acetoxybenzene (IIIId) and 2-(1-methyl-1-butenyloxy)-1-acetoxybenzene (Vd). The glc analysis of the

mixture indicated the ratio of II to III and V to be 0.75:1.85:1. A mixture fraction, after hydrolysis, analyzed by glc and hplc also showed the presence of 2,2-dibromopentane (VIId), catechol (VII), 2-pentanone (VIIIId), 2-bromo-2-pentene (IXd), 2-methyl-2-(*n*-propyl)-5-acetyl-1,3-benzodioxole (Xd).

#### 2-( $\alpha$ -Hydroxy- $\alpha$ -methylbutoxy)-1-acetoxybenzene (IIId).

This compound was obtained in 15% yield, (1.8 g), bp 67-68° (5 mm); ir (film): 3360 (OH), 1740 (C=O), 1240  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.75 (s, 4 H aromatic), 3.45 (s, 1 H, OH deuterium oxide exchanged), 2.04 (s, 3 H, O—CO—CH<sub>3</sub>), 1.90-1.64 (m, 4 H, —CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>), 1.44 (s, 3 H, >C—CH<sub>3</sub>) and 0.90-0.75 ppm (m, 3 H, CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>4</sub>: C, 65.53; H, 7.61. Found: C, 65.45; H, 7.58.

#### 2-( $\alpha$ -Bromo- $\alpha$ -methylbutoxy)-1-acetoxybenzene (IIIId).

This compound was obtained in 37% yield (5.6 g), bp 85-87° (5 mm); n<sub>D</sub><sup>25</sup> 1.5248; ir (film): 1730 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.67 (s, 4 H aromatic), 2.09 (s, 3 H, O—CO—CH<sub>3</sub>), 1.90-1.64 (m, 4 H, —CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>), 1.40 (s, 3 H, ≡C—CH<sub>3</sub>) and 0.93-0.74 ppm (t, 3 H, —CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>BrO<sub>3</sub>: C, 51.83; H, 5.69; Br, 26.57. Found: C, 52.01; H, 5.73; Br, 26.49.

#### 2-(1-Methyl-1-butenoxy)-1-acetoxybenzene (Vd).

This compound was obtained in 20% yield, (2 g), bp 135-136° (10 mm); ir (film): 1735 (C=O), 1240 (C—O), 990  $\text{cm}^{-1}$  (C=C); nmr (deuteriochloroform):  $\delta$  6.73 (s, 4 H aromatic), 5.76 (t, 1 H, =CH—C<sub>2</sub>H<sub>5</sub>), 2.05 (s, 3 H, O—CO—CH<sub>3</sub>), 1.99 (m, 2 H, —CH<sub>2</sub>—CH<sub>3</sub>), 1.61 (s, 3 H, ≡C—CH<sub>3</sub>) and 0.88 ppm (t, 3 H, CH<sub>2</sub>—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.89; H, 7.32. Found: C, 70.79; H, 7.34.

#### Cleavage of Spiro[1,3-benzodioxo-2,1'-cyclopentane] (Ie).

Cleavage of Ie (8.8 g, 50 mmoles), under the previously described conditions, gave after column chromatography on silica gel using petroleum ether 40-70°-diethyl ether (3:1), a mixture of 2-( $\alpha$ -hydroxycyclopentoxy)-1-acetoxybenzene IIe, 2-( $\alpha$ -bromocyclopentoxy)-1-acetoxybenzene (IIIe) and 2-(1-cyclopentenoxy)-1-acetoxybenzene (Ve). The glc analysis of the mixture indicated the ratio of II to III and V to be 3.7:1.8:2.1. A mixture fraction, after hydrolysis, analyzed by glc and hplc also showed the presence of catechol (VII), 1,1-dibromocyclopentane (VIe), cyclopentanone (VIIIe), 1-bromo-1-cyclopentene (IXe) and 5-acetylspiro[1,3-benzodioxo-2,1'-cyclopentane] (Xe).

#### 2-( $\alpha$ -Hydroxycyclopentoxy)-1-acetoxybenzene (IIe).

This compound was obtained in a yield of 37% (4.4 g), bp 107° (5 mm); n<sub>D</sub><sup>20</sup> 1.4279; ir (film): 3290 (OH), 1730 (C=O), 1240  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.74 (s, 4 H aromatic), 5.45 (s, 1 H, OH deuterium oxide exchanged), 2.25-1.64 (m, 8 H, —(CH<sub>2</sub>)<sub>4</sub>—) and 2.08 ppm (s, 3 H, O—CO—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>4</sub>: C, 66.08; H, 6.83. Found: C, 65.95; H, 6.86.

#### 2-( $\alpha$ -Bromocyclopentoxy)-1-acetoxybenzene (IIIe).

This compound was obtained in a yield of 18%, (2.69 g), bp 223-225° (760 mm); n<sub>D</sub><sup>25</sup> 1.5300; ir (film): 1735 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.75 (s, 4 H aromatic), 2.26-1.80 (m, 8 H, —(CH<sub>2</sub>)<sub>4</sub>—) and 2.00 ppm (s, 3 H, O—CO—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>15</sub>BrO<sub>3</sub>: C, 52.17; H, 5.02; Br, 26.75. Found: C, 52.12; H, 5.05; Br, 26.69.

#### 2-(1-Cyclopentenoxy)-1-acetoxybenzene (Ve).

This compound was obtained in a yield of 21% (2.3 g), bp 108-110° (5 mm); n<sub>D</sub><sup>25</sup> 1.3990; ir (film): 1730 (C=O), 1235 (C—O), 990  $\text{cm}^{-1}$  (C=C); nmr (deuteriochloroform):  $\delta$  6.67 (s, 4 H aromatic), 5.56 (t, 1 H, CH<sub>2</sub>—CH=C—O), 2.01 (s, 3 H, O—CO—CH<sub>3</sub>) and 1.97-1.75 ppm (m, 6 H, —CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—).

Anal. Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>3</sub>: C, 71.54; H, 6.47. Found: C, 71.61; H, 6.47.

#### Cleavage of Spiro[1,3-benzodioxo-2,1'-cyclohexane] (If).

Cleavage of If under the previously described conditions gave, after column chromatography on silica gel using petroleum ether 40-70°-diethyl ether (3:1), a mixture of 2-( $\alpha$ -hydroxycyclohexoxy)-1-acetoxybenzene (IIIf), 2-( $\alpha$ -bromocyclohexoxy)-1-acetoxybenzene (IIIIf) and 2-(1-cyclohexenoxy)-1-acetoxybenzene (Vf).

The glc analysis of the mixture indicated a ratio of II to III to V to be 1.6:1:0.8. A mixture fraction, after hydrolysis, analyzed by glc and hplc, also showed the presence of 1,1-dibromo cyclohexane (VIIf), catechol (VII), cyclohexenone (VIIIIf), 1-bromo-1-cyclohexene (IXIf) and 5-acetylspiro[1,3-benzodioxo-2,1'-cyclohexane].

#### 2-( $\alpha$ -Hydroxycyclohexoxy)-1-acetoxybenzene (IIIf).

This compound was obtained in a yield of 32%, (4 g), bp 94-96° (5 mm); n<sub>D</sub><sup>25</sup> 1.3964; ir (film): 3350 (OH), 1735 (C=O), 1235  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.67 (s, 4 H aromatic), 3.58 (s, 1 H, OH deuterium oxide exchanged), 2.01 (s, 3 H, O—CO—CH<sub>3</sub>) and 1.92-1.70 ppm (m, 10 H, —(CH<sub>2</sub>)<sub>5</sub>—).

Anal. Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>: C, 67.18; H, 7.25. Found: C, 67.05; H, 7.21.

#### 2-( $\alpha$ -Bromocyclohexoxy)-1-acetoxybenzene (IIIIf).

This compound was obtained in a yield of 20%, (3.2 g), bp 205° (760 mm); n<sub>D</sub><sup>25</sup> 1.5313; ir (film): 1740 (C=O), 1235  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.70 (s, 4 H aromatic), 2.21 (s, 3 H, O—CO—CH<sub>3</sub>) and 1.93-1.45 (m, 10 H, —(CH<sub>2</sub>)<sub>5</sub>—).

Anal. Calcd. for C<sub>14</sub>H<sub>17</sub>BrO<sub>3</sub>: C, 53.67; H, 5.43; Br, 25.55. Found: C, 53.61; H, 5.44; Br, 25.49.

#### 2-(1-Cyclohexenoxy)-1-acetoxybenzene (Vf).

This compound was obtained in a yield of 16% (1.9 g), bp 145° (760 mm); n<sub>D</sub><sup>25</sup> 1.4015; ir (film): 1740 (C=O), 1230 (C—O), 990  $\text{cm}^{-1}$  (C=C); nmr (deuteriochloroform):  $\delta$  6.83 (s, 4 H aromatic), 6.28 (t, 1 H, CH<sub>2</sub>—CH=C—O), 2.21 (s, 3 H, O—CO—CH<sub>3</sub>) and 2.10-1.58 ppm (m, 8 H, —(CH<sub>2</sub>)<sub>4</sub>—).

Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>: C, 72.39; H, 6.94. Found: C, 72.32; H, 6.92.

#### Cleavage of 2-Methyl-2-isopropyl-1,3-benzodioxole (Ig).

Cleavage of Ig under the previously described conditions gave, after distillation, a mixture of 2-( $\alpha$ -hydroxy- $\alpha$ , $\beta$ -dimethylpropoxy)-1-acetoxybenzene (IIg), 2-( $\alpha$ -bromo- $\alpha$ , $\beta$ -dimethylpropoxy)-1-acetoxybenzene (IIIg) and 2-(1,2-dimethylpropenoxy)-1-acetoxybenzene (Vg). The glc analysis of the mixture showed the ratio of II to III to V to be 1.3:1.6:2.7. A mixture fraction, after hydrolysis, analyzed by glc and hplc, also showed the presence of 3,3-dibromo-2-methylpentane (VIg), catechol (VII), 3-methyl-2-butanone (VIIIg), 2-bromo-3-methyl-2-butene (IXg) and 2-methyl-2-isopropyl-5-acetyl-1,3-benzodioxole (Xg).

#### 2-( $\alpha$ -Hydroxy- $\alpha$ , $\beta$ -dimethylpropoxy)-1-acetoxybenzene (IIg).

This compound was obtained in a yield of 13%, (1.6 g), bp 73-75° (10 mm); ir (film): 3350 (OH), 1730  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.68 (s, 4 H aromatic), 3.20 (s, 1 H, OH deuterium oxide exchanged), 2.19-1.78 (m, 1 H, CH<sub>3</sub>—CH—CH<sub>3</sub>), 2.03 (s, 3 H, O—CO—CH<sub>3</sub>), 1.40 (s, 3 H, ≡C—CH<sub>3</sub>) and 1.03-0.93 ppm (d, 6 H, CH<sub>3</sub>—CH—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: C, 65.53; H, 7.61. Found: C, 65.60; H, 7.59.

#### 2-( $\alpha$ -Bromo- $\alpha$ , $\beta$ -dimethylpropoxy)-1-acetoxybenzene (IIIg).

This compound was obtained in a yield of 16%, (2.4 g), bp 80° (5 mm); ir (film): 1735 (C=O), 1230  $\text{cm}^{-1}$  (C—O); nmr (deuteriochloroform):  $\delta$  6.70 (s, 4 H aromatic), 2.05 (s, 3 H, O—CO—CH<sub>3</sub>), 2.18-1.78 (m, 1 H, CH<sub>3</sub>—CH—CH<sub>3</sub>), 1.47 (s, 3 H, ≡C—CH<sub>3</sub>) and 1.01-0.92 ppm (d, 6 H, CH<sub>3</sub>—CH—CH<sub>3</sub>).

Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>BrO<sub>3</sub>: C, 51.82; H, 5.64; Br, 26.57. Found: C, 51.77; H, 5.63; Br, 26.52.

#### 2-(1,2-Dimethylpropenoxy)-1-acetoxybenzene (Vg).

This compound was obtained in a yield of 27%, (3 g), bp 105-107° (7 mm); ir (film): 1740 (C=O), 1235 (C—O), 940  $\text{cm}^{-1}$  (C=C); nmr (deuterio-

chloroform):  $\delta$  6.72 (s, 4 H aromatic), 2.03 (s, 3 H, O—CO—CH<sub>3</sub>), 1.91 (s, 3 H, ≡C—CH<sub>3</sub>) and 1.65 ppm (s, 6 H, 2 CH<sub>3</sub>).

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.89; H, 7.32. Found: C, 70.87; H, 7.31.

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