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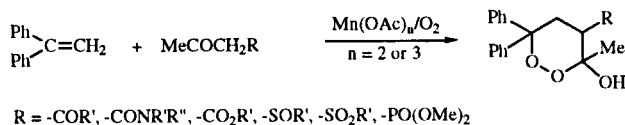
Thirteen new 2,3,5-trisubstituted furans were prepared by the acid-catalyzed decomposition of 6,6-disubstituted 1,2-dioxan-3-ols in 57-93% yields. The reaction could be accounted for as the consequence of an oxygen-oxygen bond cleavage by acid and the migration of a phenyl group at the C-6 position followed by cyclization and elimination of a phenol. The migratory aptitude was in the order of 4-MeOC₆H₄- > 4-MeC₆H₄- > Ph- > 4-FC₆H₄- > 4-ClC₆H₄- = 4-BrC₆H₄- that was found from the competitive phenyl migration in the reaction of 1,2-dioxan-3-ols bearing two different substituents at the C-6 position.

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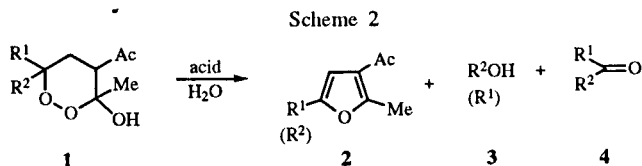
Introduction.

A number of cyclic peroxides which possess a 1,2-dioxane ring have been isolated from natural sources and have some biological activities [1-3]. We recently reported that manganous acetate (manganese(II) acetate) or manganic acetate (manganese(III) acetate)-mediated free-radical cyclization of alkenes with various active methylene compounds and air produced 1,2-dioxan-3-ol derivatives in moderate to good yields (Scheme 1) [4-9].

Scheme 1 [4-9]



Reactions of 1,2-dioxan-3-ols with triphenylphosphine and reducing reagents gave 4,5-dihydrofurans [5,7]. It was found that the treatment of the 1,2-dioxan-3-ols with strong acid yielded 2,3,5-trisubstituted furans in moderate yields [6] (Scheme 2). It should be useful if this reaction was utilized for the synthesis of substituted furans. A number of 1,2-dioxan-3-ols bearing same substituents at the C-6 position were prepared and treated with perchloric acid.



1,2-Dioxan-3-ols bearing two different aryl groups at the C-6 position were also synthesized and the migratory aptitude of the aryl groups in the acid-catalyzed reaction of the 1,2-dioxan-3-ols was investigated.

Results and Discussion.

Preparation and Acid-Catalyzed Decomposition of 6,6-Disubstituted 1,2-Dioxan-3-ols Bearing Two Identical Substituents at the C-6 Position.

6,6-Disubstituted 1,2-dioxan-3-ols were prepared by the reaction of 1,1-disubstituted ethenes with 2,4-pentanedione, acetoacetamide, methyl acetoacetate, and 1-phenylsulfonyl-2-propanone in the presence of manganese(II) or manganese(III) acetate and air. The reactions were carried out in acetic acid at a molar ratio of 1:3:1 for alkene:active methylene compound:manganese salt at 23° under a stream of dry air as reported previously [4-9]. 1,1-Diphenylethene, 1,1-bis(4-chlorophenyl)ethene, 1,1-bis(4-bromophenyl)ethene, 1,1-bis(4-fluorophenyl)ethene, 1,1-bis(4-methylphenyl)ethene, 1,1-bis(4-methoxyphenyl)ethene, 1,1-bis(2-methoxyphenyl)ethene, and 2-methylpropene were used for the preparation of 1,2-dioxan-3-ols. The newly prepared 1,2-dioxan-3-ols **1cc**, **1gg**, **1hh**, **6bb**, **8bb**, **10bb**, and **14bb** were characterized by ¹H nmr, and ir spectra, as well as elemental analyses.

The acid-catalyzed decomposition of 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols was briefly reported and known to give 2,3,5-trisubstituted furans [6]. The reaction was carried out with hydrochloric acid in acetic acid for **2a**, 76%; **2b**, 82%; and **2e**, 74%. However, 1,2-dioxan-3-ols were converted to 2,3,5-trisubstituted furans **2ag**, **7a,b**, **9a,b**, **11a,b**, and **13** more effectively by using perchloric acid in acetonitrile (Table 1).

Table 1
Acid-Catalyzed Decomposition of 1,2-Dioxan-3-ols **1** to 2,3,5-Trisubstituted Furans **2** and its Derivative **5** [a]

| Entry | Substrate | Product (yield%) [b] | Entry | Substrate | Product (yield%) |
|-------|-----------|----------------------|-------|-----------|------------------|
| 1 | | | 10 | | |
| 2 | | | 11 | | |
| 3 | | | 12 | | |
| 4 | | | 13 | | |
| 5 | | | 14 | | |
| 6 | | | 15 | | |
| 7 | | | 16 | | |
| 8 | | | 17 | | |
| 9 | | | | | |

[a] The reactions were carried out in acetonitrile containing perchloric acid at reflux temperature for 15 minutes. [b] Isolated yield after tlc separation.

It appeared that the acid-catalyzed decomposition of monocyclic 1,2-dioxan-3-ols could be a satisfactory method for the preparation of 2,3,5-trisubstituted furans, the reaction of bicyclic 1,2-dioxan-3-ols was also investigated. The decomposition of 1-hydroxy-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-7-one (**14aa**) and 4,4-bis(4-chlorophenyl)-1-hydroxy-2,3-dioxabicyclo[4.4.0]decan-7-one (**14bb**) with perchloric acid yielded 2-phenyl-6,7-dihydro-4(5*H*)-benzofuranone (**15a**) and 2-(4-chlorophenyl)-6,7-dihydro-4(5*H*)-benzofuranone (**15b**), respectively (entries 16 and 17).

Phenols **3** were also obtained and identified by compar-

ison with authentic samples, but the yields of **3** were not listed in the table because of their considerable loss during work-up procedures.

In the reaction of 4-acetyl-3,6,6-trimethyl-1,2-dioxan-3-ol (**1hh**) (entry 8), the reaction product was not a furan, but a 4,5-dihydrofuran **5**, which showed the presence of two equivalent methyl groups and another methyl group together with an acetyl group and a methylene in the ¹H nmr spectrum.

Preparation and the Acid-Catalyzed Decomposition of 1,2-Dioxan-3-ols Bearing Two Different Substituents at

Table 2
Acid-Catalyzed Decomposition of 4-Acetyl-6-(4-chlorophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ab**)

| Entry | Acid | Solvent | Temp °C | Time minutes | Product (yield/%) | | | Ratio 2b/2a [c] |
|-------|---------------------------------------|-------------------|------------|-----------------|-------------------|------------------|-----|--------------------|
| | | | | | Furans [a] | Benzophenone [b] | 4ab | |
| | | | | | 2a | 2b | 4ab | |
| 18 | HClO ₄ [d] | MeCN | reflux | 15 | 41 | 50 | | 1.2 |
| 19 | HClO ₄ | AcOH | 100 | 10 | 42 | 43 | | 1.0 |
| 20 | HClO ₄ | MeOH | reflux | 110 | 33 | 39 | | 1.2 |
| 21 | HClO ₄ | benzene | reflux | 40 | 38 | 47 | | 1.2 |
| 22 | HClO ₄ | CHCl ₃ | reflux | 30 | 41 | 41 | | 1.0 |
| 23 | HCl[e] | AcOH | 100 | 10 | 26 | 45 | 16 | 1.8 |
| 24 | HCOOH | HCOOH | 100 | 20 | 43 | 45 | 3 | 1.0 |
| 25 | H ₂ SO ₄ [f] | AcOH | 100 | 30 | 35 | 38 | 2 | 1.1 |
| 26 | BF ₃ ·Et ₂ O[g] | Et ₂ O | reflux | 240 | 29 | 30 | 20 | 1.0 |
| 27 | <i>p</i> -TsOH[h] | benzene | 50 | 120 | 42 | 43 | 3 | 1.0 |

[a] Estimated yields based on gc analysis of the mixture after tlc separation. [b] Isolated yield after tlc separation. [c] Determined by gc analysis on a crude product. [d] Perchloric acid (60%) (60 mg). [e] Concentrated hydrochloric acid (0.1 g). [f] Concentrated sulfuric acid (0.21 g). [g] Boron trifluoride etherate (2.5 ml). [h] *p*-Toluenesulfonic acid (0.17 g).

the C-6 Position.

We have investigated the different migratory aptitudes of various substituted phenyl groups at the C-6 position in 1,2-dioxan-3-ols. In order to examine the relative mobility of two different substituents at the C-6 position of 1,2-dioxan-3-ols, seventeen 1,2-dioxan-3-ols bearing two different substituents at the C-6 position and a mono substituted 1,2-dioxan-3-ol **1ai** were prepared, and their acid-catalyzed decomposition were examined (Tables 2 and 3).

Similar to the 1,2-dioxan-3-ols which have the same two substituents at the C-6 position, most of the 1,2-dioxan-3-ols bearing two different substituents at the C-6 position crystallized well and satisfactory elemental analyses have been obtained. The ¹³C nmr spectrum of 4-acetyl-6-(4-chlorophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ab**) in deuteriochloroform showed major signals assignable to one isomer, accompanied by minor signals probably due to the other. The spectrum became more complex after several hours because the intensity of the signals for the other isomer increased.

4-Acetyl-3,6-dimethyl-6-phenyl-1,2-dioxan-3-ol (**1ah**) also crystallized as a single compound and its steric structure was determined on the basis of the nuclear Overhauser effect difference experiment. The ¹H nmr spectrum of **1ah** showed the presence of two methyl groups at δ 1.15 and 1.42. The hydroxyl group at the C-3 position occupies the axial position due to the anomeric effect [11], so that the methyl group at the C-3 is equatorial, and usually appears at δ 1.3-1.4. After pre-irradiation on the two methyl groups at δ 1.15 and 1.42, the intensity of the signal for the H-4 increased by 2% and 4%, respectively. This indicated that the methyl group at the C-6 position would have an axial conformation (smaller n.o.e. value), and that the hydrogen at the C-4 position also was in the axial conformation. The ¹H nmr spectrum of **1ah** gradually

changed to that of a mixture of the two diastereomers; two new peaks appeared at δ 1.12 and 1.51 which could be assigned to methyl groups at the C-6 and C-3 position of the minor isomer, respectively (Figure 1).

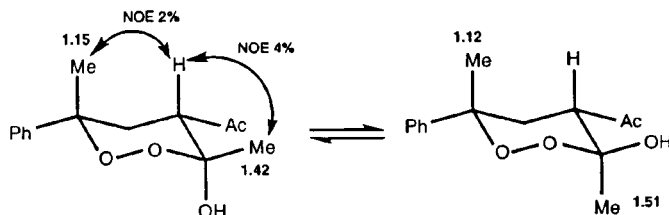


Figure 1

When **1ab** was dissolved in acetonitrile containing 60% perchloric acid and heated under reflux for 15 minutes, it gave a mixture of 3-acetyl-2-methyl-5-phenylfuran (**2a**) and 3-acetyl-5-(4-chlorophenyl)-2-methylfuran (**2b**) which were identified by comparing the ¹H nmr spectrum of the mixture with those of authentic samples. The product ratio and yields were estimated by gas chromatographic (gc) analyses on the crude product and from the intensities of appropriate peaks in the ¹H nmr spectrum when the peaks were well separated. The values obtained by the two methods usually agreed within experimental error.

The reaction was examined by changing the solvents and acids that were shown in Table 2. The yields of furans **2a** and **2b** dropped considerably and 4-chlorobenzophenone (**4ab**) was formed when hydrochloric acid and boron trifluoride were used (entries 23 and 26). The ratio of **2b/2a** was, however, changed very little except when hydrochloric acid was used (entry 23). Formic acid and *p*-

Table 3
Acid-Catalyzed Decomposition of 1,2-Dioxan-3-ols Bearing Two Different Substituents at C-6 [a]

| Entry | 1,2-Dioxan-3-ol | Furan yield/% [b] | Ratio [c] | Entry | 1,2-Dioxan-3-ol | Furan yield/% | Ratio |
|-------|-----------------|----------------------------------|-----------|-------|-----------------|------------------------------------|-------|
| 18 | | 2a (41) 2b (50) | 1.2 | 36 | | 2h (83) | — |
| 28 | | 2a (41) 2c (50) | 1.2 | 37 | | 2h (78) | — |
| 29 | | 2a (42) 2d (42) | 1.0 | 38 | | 2h (81) | — |
| 30 | | 2a (56) 2e (30) | 0.5 | 39 | | 2h (72) | — |
| 31 | | 2a (67) 2f (4) | 0.06 | 40 | | 2i (56) | — |
| 32 | | 2a (5) 2g (48) | 9.6 | 41 | | 7a (35) 7b (27) | 0.8 |
| 33 | | 2b (33) 2c (34) | 1.0 | 42 | | 9a (34) 9b (39) | 1.1 |
| 34 | | 2g (55) | — | 43 | | 11a (43) 11b (55) | 1.3 |
| 35 | | 2h (69) | — | 44 | | 15a (32) 15b (54) | 1.7 |

[a] The reactions were carried out in acetonitrile containing perchloric acid at reflux temperature for 15 minutes. [b] Yield based on the gc analysis of the mixture after tlc separation except for **2g**, **2h** and **2i**. [c] 5-Arylfuran/5-phenylfuran. Determined by gc analysis of crude products.

toluenesulfonic acid were as good as perchloric acid for the decomposition of 1,2-dioxan-3-ols, giving 2,3,5-trisubstituted furans (entries 24 and 27).

Since it seemed that perchloric acid was the best reagent to catalyze the decomposition of 1,2-dioxan-3-ols, the reactions of other 1,2-dioxan-3-ols were carried out with perchloric acid (Table 3). The acid-catalyzed decomposition of 1,2-dioxan-3-ols bearing two different substituents at the C-6 position showed that the 4-

chlorophenyl and 4-bromophenyl groups were less mobile than the phenyl group (entries 18 and 28), however, the 4-fluorophenyl group which has an electron-withdrawing fluorine atom migrated as readily as the phenyl group (entry 29). The 4-methylphenyl and the 4-methoxyphenyl groups which have an electron-releasing group migrated more readily than the phenyl group (entries 30 and 31). The 2-methoxyphenyl group was less mobile than the phenyl and 4-methoxyphenyl groups (entries 32

and 34). It is remarkable that the 2-methoxyphenyl group was far less mobile than the phenyl group.

The reactions of 6-aryl-3,6-dimethyl-1,2-dioxan-3-ols **1ah**, **1bh**, **1dh**, **1eh**, and **1fh** were also carried out which gave 3-acetyl-2,5-dimethylfuran (**2h**) (entries 35-39). As to the competition between the phenyl group and the hydrogen atom, only the phenyl group migrated in the reaction of 4-acetyl-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ai**) (entry 40). This is in contrast with the results reported by Yoshida *et al.* [10], who obtained 2-(2-benzoyl-methyl)-2-methyl-1,3-cyclopentanedione in the acid-catalyzed decomposition of 1-hydroxy-6-methyl-4-phenyl-2,3-dioxabicyclo[4.3.0]nonan-7-one.

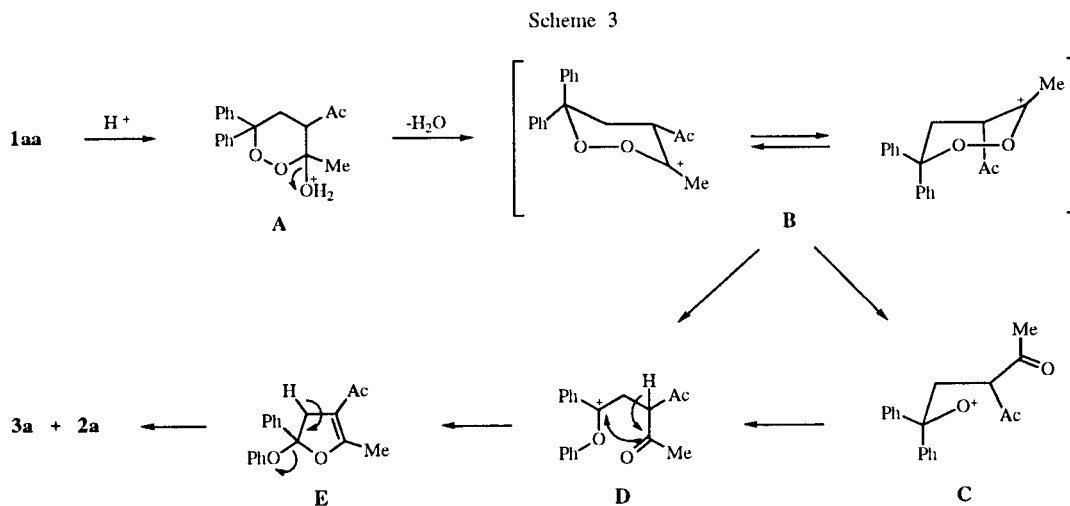
In order to examine the effect of the substituent at the C-4 position in 1,2-dioxan-3-ols on the migration of the aryl group at the C-6 position, the reactions of 4-carbamoyl-6-(4-chlorophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**6ab**), 6-(4-chlorophenyl)-3-methyl-4-(phenylcarbamoyl)-6-phenyl-1,2-dioxan-3-ol (**8ab**), and methyl 6-(4-chlorophenyl)-3-hydroxy-3-methyl-6-phenyl-1,2-dioxane-4-carboxylate (**10ab**) were carried out with perchloric acid in acetonitrile (entries 41-44). The results show that a substituent at the C-4 position in 1,2-dioxan-3-ols slightly affected the ratio of phenyl/4-chlorophenyl, but the reason is presently unclear.

tion of one of the substituents at the C-6 position takes place ($A \rightarrow B \rightarrow D$, or $A \rightarrow B \rightarrow C \rightarrow D$).

The migratory aptitude among substituted phenyl groups is rather the expected one: a phenyl group bearing an electron-donating group is more mobile than a phenyl group bearing an electron-withdrawing atom such as a halogen. If the oxygen-oxygen bond cleavage and aryl migration occur in a concerted manner ($A \rightarrow B \rightarrow D$), the migrating aryl group should be the one in the equatorial position since the antiperiplanar conformation with respect to the oxygen-oxygen bond and the equatorial aryl group is more favored in the transition state. The migrating group at the 6-position could acquire an equatorial position through a ring flipping in **B**.

Stepwise mechanism ($A \rightarrow B \rightarrow C \rightarrow D$) could not be excluded because both aryl groups are able to migrate in **C** irrespective of its original conformation in **B**. However, we think that this pathway would be less favored because it contains a positively charged oxygen. Conclusive evidence to eliminate one of these two pathways was not available. Cyclization of a cation **D** to a 4,5-dihydrofuran **E** followed by elimination of a phenol gave **2**.

In conclusion, thirteen new 2,3,5-trisubstituted furans were obtained by the acid-catalyzed decomposition of 6,6-disubstituted 1,2-dioxan-3-ols. Although several other



The Reaction Pathway.

Although the acid-catalyzed decomposition of hydroperoxides has been studied [12], the acid-catalyzed decomposition of 1,2-dioxan-3-ols leading to the formations of 2,3,5-trisubstituted furans **2** deserves comment. Protonation on the hydroxyl group at the C-3 position in **1** should be the first step in the acid-catalyzed decomposition (Scheme 3, $1 \rightarrow A$). After elimination of water from **A**, the oxygen-oxygen bond cleavage and migra-

tion of one of the substituents at the C-6 position takes place ($A \rightarrow B \rightarrow D$, or $A \rightarrow B \rightarrow C \rightarrow D$). The migratory aptitude among substituted phenyl groups is rather the expected one: a phenyl group bearing an electron-donating group is more mobile than a phenyl group bearing an electron-withdrawing atom such as a halogen. If the oxygen-oxygen bond cleavage and aryl migration occur in a concerted manner ($A \rightarrow B \rightarrow D$), the migrating aryl group should be the one in the equatorial position since the antiperiplanar conformation with respect to the oxygen-oxygen bond and the equatorial aryl group is more favored in the transition state. The migrating group at the 6-position could acquire an equatorial position through a ring flipping in **B**. Stepwise mechanism ($A \rightarrow B \rightarrow C \rightarrow D$) could not be excluded because both aryl groups are able to migrate in **C** irrespective of its original conformation in **B**. However, we think that this pathway would be less favored because it contains a positively charged oxygen. Conclusive evidence to eliminate one of these two pathways was not available. Cyclization of a cation **D** to a 4,5-dihydrofuran **E** followed by elimination of a phenol gave **2**. In conclusion, thirteen new 2,3,5-trisubstituted furans were obtained by the acid-catalyzed decomposition of 6,6-disubstituted 1,2-dioxan-3-ols. Although several other

EXPERIMENTAL

Measurements.

All of the ^1H and ^{13}C nmr spectra were taken with a JNM PMX-60SI (60 MHz) and a JNM EX-90 FT NMR (90 MHz for ^1H and 22.5 MHz for ^{13}C) spectrometer with tetramethylsilane being used as the internal standard. Chemical shifts are shown in δ values (ppm). The ir spectra were measured on a JASCO A-102 IR spectrometer and expressed in ν values (cm^{-1}). Mass spectra were measured on a JMS-DX303HF spectrometer at an ionizing voltage of 70 eV. Gas chromatography (gc) was performed on a Hewlett Packard HP5890 II gas chromatograph apparatus equipped with a flame ionization detector using a J & W. Scientific DB-5, 15 m x 0.25 mm fused silica capillary column. All of the melting-points were determined with a Yanaco micromelting-point apparatus MP-J3.

Materials.

Manganese(III) acetate dihydrate was prepared according to a method described in the literature [16]. 1,1-Diphenylethenes were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and aryl- or methylmagnesium halides. 1-Phenylsulfonyl-2-propanone was also prepared according to the literature [17]. Styrene (Wako), 2-methylpropene (Wako), 2,4-pentanedione (Wako), acetoacetamide (Aldrich), acetoacetanilide (Tokyo-Kasei), methyl acetoacetate (Wako), and 1,3-cyclohexanedione (Wako) were purchased and used as received.

Preparation of 1,2-Dioxan-3-ols 1.

The preparations of 6-substituted and 6,6-disubstituted 1,2-dioxan-3-ols **1aa**, **1al**, **1bb**, **1dd**, **1ee**, **1ff**, **6aa**, **8aa**, **10aa**, **12**, and **14aa** have been reported in previous papers [4-9]. Yields, physical properties, and analytical data of newly prepared 1,2-dioxan-3-ols are described below.

4-Acetyl-6-(4-chlorophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ab**).

This compound had mp 140° (from benzene-hexane) (91% yield); ir (chloroform): ν max 3600 (OH), 1710 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.32 (3H, s, Me), 2.30 (3H, s, Ac), 2.80 (3H, s, $-\text{CH}_2\text{CH}<$), 3.93 (1H, br s, OH), 7.13-7.67 (9H, m, arom H); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ 24.7 (Me), 29.7 (Me), 32.0 (CH_2), 52.5 ($>\text{CH}-$), 84.9 ($>\text{C}<$), 98.3 ($>\text{C}<$), 125.8 ($=\text{CH}-$), 128.3 ($=\text{CH}-$), 128.5 ($=\text{CH}-$), 128.8 ($=\text{CH}-$), 133.4 ($=\text{C}<$), 139.3 ($=\text{C}<$), 142.6 ($=\text{C}<$), 209.0 ($>\text{C}=\text{O}$).

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{ClO}_4$: C, 65.80; H, 5.52. Found: C, 65.82; H, 5.35.

4-Acetyl-6-(4-bromophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ac**).

This compound had mp 117° (from benzene-hexane) (67% yield); ir (chloroform): ν max 3580 (OH), 1700 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.40 (3H, s, Me), 2.40 (3H, s, Ac), 2.90 (3H, s, $-\text{CH}_2\text{CH}<$), 3.90-4.40 (1H, br s, OH), 7.13-7.83 (9H, m, arom H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{BrO}_4$: C, 58.32; H, 4.90. Found: C, 58.61; H, 4.93.

4-Acetyl-6-(4-fluorophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ad**).

This compound had mp 124° (from benzene-hexane) (95% yield); ir (chloroform): ν max 3584 (OH), 1698 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.31 (3H, s, Me), 2.31 (3H, s, Ac), 2.85 (3H, s, $-\text{CH}_2\text{CH}<$), 3.62 (1H, br s, OH), 6.71-7.52 (9H, m, arom H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{FO}_4$: C, 69.08; H, 5.80. Found: C, 68.83; H, 5.82.

4-Acetyl-6-(4-methylphenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ae**).

This compound had mp 99° (from benzene-hexane) (90% yield); ir (chloroform): ν max 3580 (OH), 1698 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.37 (3H, s, Me), 2.37 (6H, s, Me, Ac), 2.90 (3H, s, $-\text{CH}_2\text{CH}<$), 3.30-4.00 (1H, br s, OH),

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_4$: C, 73.60; H, 6.79. Found: C, 73.72; H, 6.86.

4-Acetyl-6-(4-methoxyphenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1af**).

This compound had mp 97° (from diethyl ether-hexane) (74% yield); ir (chloroform): ν max 3575 (OH), 1700 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.35 (3H, s, Me), 2.35 (3H, s, Ac), 2.87 (3H, s, $-\text{CH}_2\text{CH}<$), 3.80 (3H, s, OMe), 4.00-4.77 (1H, br s, OH), 6.67-7.70 (9H, m, arom H).

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_5$: C, 70.16; H, 6.48. Found: C, 70.06; H, 6.68.

4-Acetyl-6-(2-methoxyphenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**1ag**).

This compound had mp 122° (from benzene-hexane) (89% yield); ir (chloroform): ν max 3440 (OH), 1711 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.30 (0.8H, s, Me), 1.40 (2.2H, s, Me), 2.40 (2.2H, s, Ac), 2.45 (0.8H, s, Ac), 2.50-3.50 (3H, m, $-\text{CH}_2\text{CH}<$), 3.68 (1H, br s, OH), 3.78 (0.8H, s, OMe), 3.80 (1.1H, s, OMe), 4.00 (1.1H, s, OMe), 6.78-7.70 (9H, m, arom H).

Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_5$: C, 70.16; H, 6.48. Found: C, 70.35; H, 6.56.

4-Acetyl-3,6-dimethyl-6-phenyl-1,2-dioxan-3-ol (**1ah**).

This compound had mp 116° (from benzene-hexane) (73% yield); ir (chloroform): ν max 3404 (OH), 1704 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.15 (3H, s, Me), 1.42 (3H, s, Me), 1.92-2.62 (2H, m, CH_2), 2.40 (3H, s, Ac), 3.27 (1H, dd, $J = 4, 13$ Hz, $>\text{CH}-$), 3.94 (1H, br s, OH), 7.20-7.52 (5H, m, Ph).

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25. Found: C, 67.11; H, 7.51.

4-Acetyl-6-(4-bromophenyl)-6-(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (**1bc**).

This compound had mp 170° (from benzene-hexane) (44% yield); ir (chloroform): ν max 3436 (OH), 1700 (Ac); ^1H nmr (60 MHz, DMSO- d_6): δ 1.40 (3H, s, Me), 2.37 (3H, s, Ac), 2.63-3.40 (3H, m, $-\text{CH}_2\text{CH}<$), 4.50-4.90 (1H, br s, OH), 7.02-7.70 (8H, m, arom H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{BrClO}_4$: C, 53.61; H, 4.26. Found: C, 53.84; H, 4.20.

4-Acetyl-6-(4-chlorophenyl)-3,6-dimethyl-1,2-dioxan-3-ol (**1bh**).

This compound was obtained as a colorless liquid (53% yield); ir (chloroform): ν max 3592 (OH), 1708 (Ac); ^1H nmr

(60 MHz, deuteriochloroform): δ 1.15 (0.6H, s, Me), 1.25 (2.4H, s, Me), 1.40 (2.4H, s, Me), 1.49 (0.6H, s, Me), 2.08-2.93 (3H, m, $-\text{CH}_2\text{CH}<$), 2.25 (2.4H, s, Ac), 2.37 (0.6H, s, Ac), 4.17 (1H, br s, OH), 7.20-7.50 (4H, m, arom H).

4-Acetyl-6,6-bis(4-bromophenyl)-3-methyl-1,2-dioxan-3-ol (**1cc**).

This compound had mp 176° (from benzene-hexane) (83% yield); ir (potassium bromide): ν max 3440 (OH), 1700 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.32 (3H, s, Me), 2.30 (3H, s, Ac), 2.49-3.07 (3H, m, $-\text{CH}_2\text{CH}<$), 4.07 (1H, br s, OH), 7.00-7.73 (8H, m, arom H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{Br}_2\text{O}_4$: C, 48.54; H, 3.86. Found: C, 48.60; H, 3.80.

4-Acetyl-6-(4-fluorophenyl)-3,6-dimethyl-1,2-dioxan-3-ol (**1dh**).

This compound was obtained as a colorless liquid (42% yield); ir (chloroform): ν max 3592 (OH), 1706 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.15 (0.7H, s, Me), 1.23 (2.3H, s, Me), 1.40 (2.3H, s, Me), 1.47 (0.7H, s, Me), 2.00-3.02 (3H, m, $-\text{CH}_2\text{CH}<$), 2.22 (2.3H, s, Ac), 2.33 (0.7H, s, Ac), 4.20 (1H, br s, OH), 6.73-7.53 (4H, m, arom H).

4-Acetyl-6-(4-methylphenyl)-3,6-dimethyl-1,2-dioxan-3-ol (**1eh**).

This compound was obtained as a colorless liquid (46% yield); ir (chloroform): ν max 3411 (OH), 1707 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.15 (0.7H, s, Me), 1.23 (2.3H, s, Me), 1.37 (2.3H, s, Me), 1.49 (0.7H, s, Me), 1.97-2.97 (3H, m, $-\text{CH}_2\text{CH}<$), 2.08 (3H, s, Me), 2.18 (2.3H, s, Ac), 2.27 (0.7H, s, Ac), 3.93 (1H, br s, OH), 7.07-7.53 (4H, m, arom H).

4-Acetyl-6-(2-methoxyphenyl)-6-(4-methoxyphenyl)-3-methyl-1,2-dioxan-3-ol (**1fg**).

This compound had mp 147° (from benzene) (90% yield); ir (chloroform): ν max 3592 (OH), 1704 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.17 (2.3H, s, Me), 1.28 (0.7H, s, Me), 2.28 (0.7H, s, Ac), 2.33 (2.3H, s, Ac), 2.0-3.6 (3H, m, $-\text{CH}_2\text{CH}<$), 3.50 (6H, s, 2 x OMe), 3.75-4.35 (1H, br s, OH), 6.20-7.50 (8H, m, arom H).

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_6$: C, 67.73; H, 6.50. Found: C, 67.42; H, 6.26.

4-Acetyl-6-(4-methoxyphenyl)-3,6-dimethyl-1,2-dioxan-3-ol (**1fh**).

This compound was obtained as a colorless liquid (40% yield); ir (chloroform): ν max 3588 (OH), 1705 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.17 (0.7H, s, Me), 1.25 (2.3H, s, Me), 1.40 (2.3H, s, Me), 1.48 (0.7H, s, Me), 2.01-2.93 (3H, m, $-\text{CH}_2\text{CH}<$), 2.25 (2.3H, s, Ac), 2.35 (0.7H, s, Ac), 3.80 (3H, s, OMe), 4.13 (1H, br s, OH), 6.77-7.53 (4H, m, arom H).

4-Acetyl-6,6-bis(2-methoxyphenyl)-3-methyl-1,2-dioxan-3-ol (**1gg**).

This compound had mp 141° (from benzene-hexane) (78% yield); ir (potassium bromide): ν max 3452 (OH), 1704 (Ac); ^1H nmr (60 MHz, deuteriochloroform): δ 1.18 (0.7H, s, Me), 1.30 (2.3H, s, Me), 2.20 (2.3H, s, Ac), 2.27 (0.7H, s, Ac), 2.51-3.51 (3H, m, $-\text{CH}_2\text{CH}<$), 3.42 (0.7H, s, OMe), 3.51 (0.7H, s, OMe), 3.67 (2.3H, s, OMe), 3.83 (2.3H, s, OMe), 5.33 (1H, br s, OH),

6.57-7.83 (8H, m, arom H).

Anal. Calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_6$: C, 67.73; H, 6.50. Found: C, 68.03; H, 6.50.

4-Acetyl-3,3,6-trimethyl-1,2-dioxan-3-ol (**1hh**).

This compound had mp 92° (from hexane) (20% yield); ir (chloroform): ν max 3416 (OH), 1699 (Ac); ^1H nmr (400 MHz, deuteriochloroform): δ 1.26 (2.5H, s, Me), 1.41 (6H, s, 2 x Me), 1.60 (0.5H, s, Me), 1.57-2.23 (2H, m, CH_2), 2.26 (2.5H, s, Ac), 2.33 (0.5H, s, Ac), 2.97-3.21 (1H, m, $>\text{CH}<$), 4.03 (1H, s, OH).

Anal. Calcd. for $\text{C}_9\text{H}_{16}\text{O}_4$: C, 57.43; H, 8.57. Found: C, 57.76; H, 8.66.

4-Carbamoyl-6-(4-chlorophenyl)-3-methyl-6-phenyl-1,2-dioxan-3-ol (**6ab**).

This compound had mp 205° (from benzene-hexane) (64% yield); ir (potassium bromide): ν max 3672-3444 (OH and NH_2), 1642 (CONH_2); ^1H nmr (60 MHz, $\text{DMSO}-d_6$): δ 1.30 (2.1H, s, Me), 1.53 (0.9H, s, Me), 2.10-3.10 (3H, m, $-\text{CH}_2\text{CH}<$), 3.20-3.77 (1H, br s, OH), 6.83-7.33 (2H, br s, NH_2), 7.33-7.87 (9H, m, arom H).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{ClNO}_4$: C, 62.16; H, 5.22; N, 4.03. Found: C, 62.07; H, 5.21; N, 4.04.

4-Carbamoyl-6,6-bis(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (**6bb**).

This compound had mp 157-158° (from benzene) (87% yield); ir (chloroform): ν max 3450-3180 (OH and NH_2), 1646 (CONH_2); ^1H nmr (60 MHz, $\text{DMSO}-d_6$): δ 1.25 (2.5H, s, Me), 1.45 (0.5H, s, Me), 2.13-3.02 (3H, m, $-\text{CH}_2\text{CH}<$), 6.82-7.20 (1H, br s, OH), 7.17 (2H, br, NH_2), 7.19-7.68 (8H, m, arom H).

Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}_4$: C, 56.56; H, 4.48; N, 3.66. Found: C, 56.96; H, 4.54; N, 3.64.

6-(4-Chlorophenyl)-3-methyl-4-(phenylcarbamoyl)-6-phenyl-1,2-dioxan-3-ol (**8ab**).

This compound had mp 193° (from ethanol) (78% yield); ir (potassium bromide): ν max 3600-3260 (OH and NH), 1653 (CONH); ^1H nmr (60 MHz, $\text{DMSO}-d_6$): δ 1.26 (2.3H, s, Me), 1.50 (0.7H, s, Me), 2.42-3.17 (3H, m, $-\text{CH}_2\text{CH}<$), 6.81 (1H, br s, OH), 6.90-7.98 (14H, m, arom H), 9.78 (1H, br s, NH).

Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{ClNO}_4$: C, 68.00; H, 5.23; N, 3.31. Found: C, 67.88; H, 5.32; N, 3.35.

6,6-Bis(4-chlorophenyl)-3-methyl-4-(phenylcarbamoyl)-1,2-dioxan-3-ol (**8bb**).

This compound had mp 163-164° (from benzene) (93% yield); ir (potassium bromide): ν max 3226-2956 (OH and NH), 1656 (CONH); ^1H nmr (60 MHz, $\text{DMSO}-d_6$): δ 1.28 (2.4H, s, Me), 1.53 (0.6H, s, Me), 2.62-3.20 (3H, m, $-\text{CH}_2\text{CH}<$), 6.85 (0.8H, s, OH), 7.05 (0.2H, s, OH), 7.09-7.83 (13H, m, arom H), 9.77 (1H, br s, NH).

Anal. Calcd. for $\text{C}_{24}\text{H}_{21}\text{Cl}_2\text{NO}_4$: C, 62.89; H, 4.62; N, 3.05. Found: C, 62.97; H, 4.78; N, 2.81.

Methyl 6-(4-Chlorophenyl)-3-hydroxy-3-methyl-6-phenyl-1,2-dioxane-4-carboxylate (**10ab**).

This compound had mp 183° (from benzene-hexane) (72% yield); ir (chloroform): ν max 3588 (OH), 1734 (COOMe); ^1H nmr (60 MHz, deuteriochloroform): δ 1.48 (3H, s, Me), 2.93 (3H, s, $-\text{CH}_2\text{CH}<$), 3.83 (3H, s, COOMe), 3.84-4.13 (1H, br s,

OH), 7.26-7.67 (9H, m, arom H).

Anal. Calcd. for $C_{19}H_{19}ClO_5$: C, 62.90; H, 5.28. Found: C, 62.81; H, 5.35.

Methyl 6,6-Bis(4-chlorophenyl)-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate (**10bb**).

This compound had mp 173° (from hexane) (89% yield); ir (potassium bromide): ν max 3490 (OH), 1738 (COOMe); 1H nmr (60 MHz, deuteriochloroform): δ 1.41 (3H, s, Me), 2.89 (3H, s, $-CH_2CH<$), 3.74 (3H, s, OMe), 7.15 (4H, s, arom H), 7.45 (4H, s, arom H).

Anal. Calcd. for $C_{19}H_{18}Cl_2O_5$: C, 57.44; H, 4.57. Found: C, 57.41; H, 4.59.

4-(4-Chlorophenyl)-1-hydroxy-4-phenyl-2,3-dioxabicyclo[4.4.0]decan-7-one (**14ab**).

This compound had mp 159° (from benzene-hexane) (72% yield); ir (chloroform): ν max 3372 (OH), 1720 ($>C=O$); 1H nmr (60 MHz, deuteriochloroform): δ 1.42-2.80 (9H, m, 3 x CH_2 and $-CH_2CH<$), 3.30-3.80 (1H, br s, OH), 7.15-7.60 (9H, m, arom H).

Anal. Calcd. for $C_{20}H_{19}ClO_4$: C, 66.95; H, 5.34. Found: C, 66.90; H, 5.47.

4,4-Bis(4-chlorophenyl)-1-hydroxy-2,3-dioxabicyclo[4.4.0]decan-7-one (**14bb**).

This compound had mp 176° (from benzene-hexane) (45% yield); ir (potassium bromide): ν max 3500 (OH), 1723 ($>C=O$); 1H nmr (60 MHz, DMSO- d_6): δ 2.30-2.75 (10H, m, 3 x CH_2 , $-CH_2CH<$, OH), 7.18-7.68 (8H, m, arom H).

Anal. Calcd. for $C_{20}H_{18}Cl_2O_4$: C, 61.08; H, 4.61. Found: C, 61.25; H, 4.63.

Acid-Catalyzed Decomposition of 1,2-Dioxan-3-ols **1aa-ii**, **1ab-ai**, **1bc**, **1bh**, **1dh**, **1eh**, **1fg**, **1fh**, **6aa**, **6ab**, **6bb**, **8aa**, **8ab**, **8bb**, **10aa**, **10ab**, **10bb**, **12**, **14aa**, **14ab**, and **14bb**.

A typical procedure for the acid-catalyzed decomposition of 1,2-dioxan-3-ols is as follows. A solution of a 1,2-dioxan-3-ol (1 mmole) in acetonitrile (15 ml) containing an acid (0.36-2.1 mmoles) was heated under reflux for 15 minutes. The reaction was quenched with water (60 ml) and the reaction mixture was extracted with diethyl ether (2 x 30 ml). The extract was washed with water (20 ml), dried (magnesium sulfate), and evaporated. The residue was chromatographed on a silica gel plate while eluting with chloroform or benzene. In the cases of **7a,b** and **9a,b** the crude product crystallized, when the reaction mixture was poured into ice water. The yields are listed in Tables 1-3. The products were further purified by recrystallization to obtain analytical samples. Physical properties of the furans, which were obtained in a pure state, are described below.

3-Acetyl-2-methyl-5-phenylfuran (**2a**).

This compound had mp $50-51^\circ$ (from hexane) (lit mp $50-51^\circ$ [6]).

3-Acetyl-5-(4-chlorophenyl)-2-methylfuran (**2b**).

This compound had mp $112-114^\circ$ (from hexane) (lit mp $112-114^\circ$ [6]).

3-Acetyl-5-(4-bromophenyl)-2-methylfuran (**2c**).

This compound had mp 114° (from hexane); ir (chloroform): ν max 1673 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 2.42

(3H, s, Ac), 2.63 (3H, s, Me), 6.85 (1H, s, $=CH-$), 7.50 (4H, s, arom H).

Anal. Calcd. for $C_{13}H_{11}BrO_2$: C, 55.96; H, 3.97. Found: C, 56.10; H, 4.05.

3-Acetyl-5-(4-fluorophenyl)-2-methylfuran (**2d**).

This compound had mp 92° (from hexane); ir (potassium bromide): ν max 1676 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 2.42 (3H, s, Ac), 2.63 (3H, s, Me), 6.75 (1H, s, $=CH-$), 6.88-7.80 (4H, m, arom H).

Anal. Calcd. for $C_{13}H_{11}FO_2$: C, 71.58; H, 5.04. Found: C, 71.55; H, 5.13.

3-Acetyl-5-(4-methylphenyl)-2-methylfuran (**2e**).

This compound had mp $61-63^\circ$ (from hexane) (lit mp $61-63^\circ$ [6]).

3-Acetyl-5-(4-methoxyphenyl)-2-methylfuran (**2f**).

This compound had mp 92° (from hexane); ir (potassium bromide): ν max 1674 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 2.40 (3H, s, Ac), 2.62 (3H, s, Me), 3.82 (3H, s, OMe), 6.67 (1H, s, $=CH-$), 6.88 (2H, m, arom H), 7.53 (2H, m, arom H).

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.96; H, 6.24.

3-Acetyl-5-(2-methoxyphenyl)-2-methylfuran (**2g**).

This compound had mp 85° (from hexane); ir (potassium bromide): ν max 1665 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 2.44 (3H, s, Ac), 2.63 (3H, s, Me), 3.93 (3H, s, OMe), 7.10 (1H, s, $=CH-$), 6.93-7.80 (4H, m, arom H).

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.37; H, 6.27.

3-Acetyl-2,5-dimethylfuran (**2h**).

This compound was obtained as a colorless liquid [18]; ir (chloroform): ν max 1665 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 2.23 (3H, s, Me), 2.37 (3H, s, Ac), 2.53 (3H, s, Me), 6.20 (1H, s, $=CH-$).

3-Acetyl-2-methylfuran (**2i**).

This compound was obtained as a colorless liquid (lit bp $84-87^\circ/12$ mm Hg [19]); ir (chloroform): ν max 1671 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 2.38 (3H, s, Ac), 2.57 (3H, s, Me), 6.62 (1H, d, $J = 2.2$ Hz, H-4), 7.23 (1H, d, $J = 2.2$ Hz, H-5).

3-Acetyl-2,5,5-trimethyl-4,5-dihydrofuran (**5**).

This compound was obtained as a colorless liquid; ir (chloroform): ν max 1707 (Ac); 1H nmr (60 MHz, deuteriochloroform): δ 1.38 (6H, s, 2 x Me), 2.17 (3H, s, Ac), 2.19 (3H, t, $J = 1.6$ Hz, Me), 2.73 (2H, q, $J = 1.6$ Hz, CH_2).

Anal. Calcd. for $C_9H_{14}O_2$: M, 154.0994. Found: m/z 154.0973.

3-Carbamoyl-2-methyl-5-phenylfuran (**7a**).

This compound had mp 191° dec (from ethyl acetate-hexane); ir (potassium bromide): ν max 3170 ($-NH_2$), 1665 and 1614 ($CONH_2$); 1H nmr (60 MHz, deuteriochloroform): δ 2.25 (3H, s, Me), 6.15 (1H, d, $J = 2.2$ Hz, $=CH-$, collapsed to a singlet on deuteration), 7.20-7.23 (5H, m, Ph), 8.34 (2H, br s, NH_2).

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.39; H, 5.53; N, 6.92.

3-Carbamoyl-5-(4-chlorophenyl)-2-methylfuran (7b).

This compound had mp 214° dec (from ethyl acetate-hexane); ir (potassium bromide): ν max 3160 (NH₂), 1675 and 1630 (CONH₂); ¹H nmr (90 MHz, acetone-d₆): δ 2.27 (3H, s, Me), 6.56 (1H, d, J = 2.3 Hz, =CH-, collapsed to a singlet on deuteration), 7.31-7.75 (4H, m, arom H), 8.01 (2H, br s, NH₂).

Anal. Calcd. for C₁₂H₁₀ClNO₂: C, 61.16; H, 4.28; N, 5.94. Found: C, 61.23; H, 4.26; N, 5.98.

2-Methyl-3-(phenylcarbamoyl)-5-phenylfuran (9a).

This compound had mp 141° (from hexane); ir (chloroform): ν max 1659 (CONH); ¹H nmr (60 MHz, deuteriochloroform): δ 2.28 (3H, s, Me), 6.08 (1H, s, =CH-), 6.93-7.40 (10H, m, 2 x Ph), 9.0 (1H, br s, NH).

Anal. Calcd. for C₁₈H₁₅NO₂: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.87; H, 5.46; N, 4.94.

5-(4-Chlorophenyl)-2-methyl-3-(phenylcarbamoyl)furan (9b).

This compound had mp 145° (from hexane); ir (potassium bromide): ν max 1639 (CONH); ¹H nmr (60 MHz, DMSO-d₆): δ 2.28 (3H, s, Me), 6.13 (1H, s, =CH-), 6.90-7.47 (9H, m, arom H), 9.33 (1H, br s, NH).

Anal. Calcd. for C₁₈H₁₄ClNO₂: C, 69.35; H, 4.53; N, 4.49. Found: C, 69.59; H, 4.64; N, 4.42.

Methyl 2-Methyl-5-phenylfuran-3-carboxylate (11a).

This compound had mp 65° (from hexane); ir (potassium bromide): ν max 1710 (COOMe); ¹H nmr (60 MHz, deuteriochloroform): δ 2.62 (3H, s, Me), 3.85 (3H, s, OMe), 6.90 (1H, s, =CH-), 7.3-7.9 (5H, m, Ph).

Anal. Calcd. for C₁₃H₁₂O₃: C, 72.21; H, 5.59. Found: C, 72.12; H, 5.61.

Methyl 5-(4-Chlorophenyl)-2-methylfuran-3-carboxylate (11b).

This compound had mp 109.5° (from hexane); ir (potassium bromide): ν max 1710 (COOMe); ¹H nmr (60 MHz, deuteriochloroform): δ 2.62 (3H, s, Me), 3.85 (3H, s, OMe), 6.87 (1H, s, =CH-), 7.27-7.66 (4H, m, arom H).

Anal. Calcd. for C₁₃H₁₁ClO₃: C, 62.29; H, 4.42. Found: C, 62.26; H, 4.45.

2-Methyl-3-(phenylsulfonyl)-5-phenylfuran (13).

This compound had mp 117° (from hexane); ir (chloroform): ν max 1318 and 1158 (>SO₂); ¹H nmr (400 MHz, deuteriochloroform): δ 2.67 (3H, s, Me), 6.79 (1H, s, =CH-), 7.26-7.98 (10H, m, 2 x Ph).

Anal. Calcd. for C₁₇H₁₄O₃S: C, 68.44; H, 4.73. Found: C, 68.79; H, 4.79.

2-Phenyl-6,7-dihydro-4(5H)-benzofuranone (15a).

This compound had mp 139-140° (from hexane); ir (potassium bromide): ν max 1668 (>C=O); ¹H nmr (60 MHz, deuteriochloroform): δ 2.0-2.7 (4H, m, CH₂CH₂), 2.94 (2H, t, J = 5.8 Hz, CH₂), 6.93 (1H, s, =CH-), 7.2-7.8 (5H, m, Ph).

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.23; H, 5.69. Found: C, 78.85; H, 5.69.

2-(4-Chlorophenyl)-6,7-dihydro-4(5H)-benzofuranone (15b).

This compound had mp 128° (from hexane); ir (potassium bromide): ν max 1668 (>C=O); ¹H nmr (60 MHz, deuteriochloroform): δ 2.23 (2H, m, CH₂), 2.55 (2H, t, CH₂), 2.96 (2H, t, CH₂), 6.89 (1H, s, =CH-), 7.29-7.66 (4H, m, arom H).

Anal. Calcd. for C₁₄H₁₁ClO₂: C, 68.16; H, 4.50; Found: C, 68.19; H, 4.55.

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