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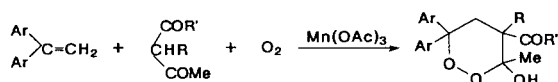
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The reactions of β -keto sulfoxide, β -keto sulfones, or β -keto phosphinate with 1,1-disubstituted ethenes in the presence of manganese(III) acetate and molecular oxygen yielded 4-phenylsulfanyl-, 4-phenylsulfonyl-, or 4-phosphinoyl-1,2-dioxan-3-ols **3** in moderate-to-good yields. *m*-Chloroperbenzoic acid oxidation of 4-phenylsulfanyl-1,2-dioxan-3-ols gave the corresponding 4-phenylsulfonyl derivatives. The temperature dependence of the reactions was observed and the stereochemistry of the 1,2-dioxan-3-ols are discussed.

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We recently reported manganous acetate (manganese(II) acetate) or manganese(III) acetate (manganic acetate)-mediated oxidative free-radical cyclization of alkenes with 1,3-diones [1-3], β -keto esters [1] or acetoacetamides [4], and molecular oxygen that yielded 1,2-dioxan-3-ols in good yields (Scheme 1). It was found that the reaction of alkenes with acetoacetamide and oxygen in the presence of manganese(III) acetate gave 1,2-dioxan-3-ols most effectively [4]. The use of manganese(II) acetate on the other hand improved the yields in the reaction of alkenes with active methine compounds and oxygen [3]. It should be interesting to extend the reaction to the synthesis of sulfur-, sulfoxide-, sulfone, or phosphinate-containing 1,2-dioxan-3-ols, which may have biological activities [5], and the results are described in this paper.

Scheme 1



R=H, alkyl
R'=alkyl, -N-, -O-

Results and Discussion.

Reactions of Phenylsulfanyl-2-propanone (**1a**) with 1,1-Disubstituted Ethenes **2a-f**.

When the reaction of phenylsulfanyl-2-propanone (**1a**) with 1,1-diphenylethene (**2a**) was carried out in the presence of manganese(III) acetate at a molar ratio of 1:1:1 under a current of dry-air at 32°, the major product was found to be 3-methyl-4-(phenylsulfanyl)-6,6-diphenyl-1,2-dioxan-3-ol (**3aa**) together with benzophenone (**4a**) and 2,2-diphenyl-2-hydroxyethyl acetate (**5a**) as minor products (Scheme 2, entry 2). The structural assignments are based on the ¹H nmr, ¹³C nmr, and ir spectra, as well as ele-

mental analysis. The yield of **3aa** was slightly improved either by increasing the molar ratio of **1a** or [manganese(II) acetate] (entries 3 and 7-9), but **1a** was recovered in the reaction at a higher molar ratio of **1a** (entries 3 and 4). The reaction at a higher temperature not only gave a decreased yield of **3aa**, but also resulted in the formation of 2-methyl-3-(phenylsulfanyl)-5,5-diphenyl-4,5-dihydrofuran (**6aa**) (entry 11). When the ¹H nmr spectrum of **3aa** was measured in deuteriochloroform two methyl signals appeared at δ 1.73 and 2.08 with different intensities. This would indicate that the compound is a mixture of two stereoisomers, which could not be separated either by chromatography or by recrystallization. Then, the isomer ratio was determined from the intensities of the two methyl signals and is shown in Table 2. The methylene group and the methyl group in **6aa** are shown as an ABX₃ spin system with $J_{AB} = 14.4$ Hz and $J_{AX} = J_{BX} = 1.6$ Hz in its ¹H nmr spectrum. The non-equivalence of the two hydrogens on the methylene is probably due to the presence of a chiral phenylsulfanyl group at the C-3 position. Then we have examined the reactions using other metal acetates such as manganese(II) acetate, cobalt(II) acetate, cobalt(III) acetate, and ceric ammonium nitrate (CAN). However, all these salts except for CAN failed to give products and only starting materials were recovered. The reaction with CAN gave **3aa** and **6aa** in moderate yields (entry 12).

Then, the reactions were examined for 1,1-bis(4-chlorophenyl)ethene (**2b**), 1,1-bis(4-methylphenyl)ethene (**2c**), 1,1-bis(4-fluorophenyl)ethene (**2d**), 1,1-bis(4-methoxyphenyl)ethene (**2e**), and 2-ethyl-1-butene (**2f**) (Scheme 2, Table 2). A 1:1:1.5 molar ratio for **1a**:**2**:manganese(III) acetate was chosen for further investigation since it gave the best yield for 1,2-dioxan-3-ols as shown in Table 1. The reactions with 1,1-diaryl substituted ethenes **2b-e** and 1,1-dialkyl substituted ethene **2f** gave the corresponding 3-methyl-4-(phenylsulfanyl)-1,2-dioxan-3-ols **3ab-af** in moderate-to-

Table 3
Reactions of (4-Methylphenyl)sulfonyl-2-propanone (**1c**) with 1,1-Diphenylethene (**2a**) and Manganese (III) Acetate-Oxygen

Entry	Molar ratio [a]	Temperature °C	Time hours	Composition of product (yield/%) [b]					
				1c	2a	3ca	4a	5a	6ca
18	1:1:1	35	24	92	86		2	6	
19	1:1.2:1	50	10	19	23	38	12	10	16
20	1:1.5:2	55	11		15	49	14	6	24
21	1:1.2:2	48	16			58	8	4	15
22	1:1.2:2	42	20	56	43	28	17	10	28
23	1:1.2:3	48	14			52	11	2	19

[a] **1c**:**2a**: $[\text{Mn}(\text{OAc})_3]$. [b] Isolated yields based on the amount of **1c** used.

Table 4
Reactions of β -Keto Sulfones **1b** and **1c** and Dimethoxyphosphinoyl-2-propanone (**1d**) with 1,1-Disubstituted Ethenes **2a-c** and Manganese (III) Acetate-Oxygen [a]

Entry	β -Keto compound	Alkene	Temperature °C	Time hours	Composition of product (yield/%) [b]				Isomer ratio of 3
					3ba	4a	5a	6ba	
24	1b	2a	48	16	3ba (52)	4a (18)	5a (6)	6ba (17)	85:15
25	1b	2b	48	15	3bb (47)	4b (8)	5b (18)	6bb (11)	87:13
26	1b	2c	48	10	3bc (63)	4c (12)	5c (12)	6bc (9)	89:11
21	1c	2a	48	16	3ca (58)	4a (8)	5a (4)	6ca (15)	86:14
27	1d	2a	40	12	3da (46)	4a (9)	5a (2)	6da (21)	

[a] The reactions were carried out in acetic acid at a 1:1.2:2 molar ratio for **1**: $[\text{Mn}(\text{OAc})_3]$ under a current of dry-air. [b] Yields for **4** and **5** are based on the amount of **2** used, and yields for **3** and **6** are based on the amount of **1** used.

Table 5
Reactions of β -Keto Compounds **1a-d** with 1,1-Disubstituted Ethenes **2a-c** in the Presence of Manganese (III) Acetate in Acetic Acid at 80°

Entry	β -Keto compound	Alkene	Molar ratio [a]	Time minutes	Composition of product (yield/%) [b]			
					1a	2a	4a	6aa
28	1a	2a	1:1:2	180	1a (18)	2a (23)	4a (3)	6aa (62)
29	1a	2a	1:1:4	12	1a (12)	2a (14)	4a (2)	6aa (76)
30	1a	2a	1:1:4	60			4a (6)	6aa (83)
31	1a	2b	1:1:5	30			4b (8)	6ab (78)
32	1b	2a	1:1:4	84			4a (2)	6ba (88)
33	1b	2b	1:1:4	30			4b (6)	6bb (80)
34	1b	2c	1:1:4	30			4c (11)	6bc (82)
35	1c	2a	1:1:4	30			4a (9)	6ca (77)
36	1d	2a	1:1:4	30			4a (14)	6da (68)

[a] β -Keto compound: Alkene: $[\text{Mn}(\text{OAc})_3]$. [b] Isolated yields based on the amount of **1** added.

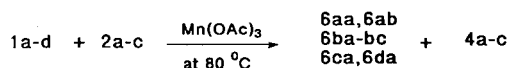
ganese(III) acetate in acetic acid under a dry-air stream at 35° practically did not take place (Table 3, entry 18), so that the reactions were carried out at higher temperatures. At a temperature between 42° and 55°, the reaction yielded 4-(4-methylphenyl)sulfonyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3ca**) together with 3-(4-methylphenyl)sulfonyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**6ca**) (Scheme 2, Table 3, entries 19-23). Similar reactions of alkenes **2b** and **2c** with **1b** were carried out at 48° at a molar ratio of 1:1.2:2, and the results are shown in Scheme 2 and Table 4. 4-Arylsulfonyl-1,2-dioxan-3-ols **3ba-bc** and **3ca** were obtained as a mixture of two stereoisomers that were observed by ¹H and ¹³C nmr spectra. The isomer ratio was determined again from the intensity of the methyl signals

which appeared at δ 1.8-2.0 in the ¹H nmr spectra. The methylene group and methyl group in **6ca** are shown as an A₂X₃ spin system with J_{AX} = 1.8 Hz.

As the composition of products significantly changed depending on the reaction temperature, the reactions of phenylsulfonyl-2-propanone (**1a**) and arylsulfonyl-2-propanones **1b** and **1c** with 1,1-diarylethenes **2a-c** were investigated at 80°. A mixture of stoichiometric amounts of **1a**, **2a** and manganese(III) acetate to form **6aa** (1:1:2) was heated at 80° for 180 minutes, but considerable amounts of **1a** and **2a** were recovered unchanged along with **6aa** (Table 5, entry 28). With using 4 equivalents of manganese(III) acetate and for a short period of time the reaction still gave starting materials (entry 29). Thus, the reactions

were conducted thereafter at a molar ratio of 1:1:4 or 1:1:5 at 80° until the dark brown color of the reaction mixture disappeared. The results are summarized in Scheme 3 and Table 5. 4,5-Dihydrofuran derivatives **6** were obtained in good yields, but the formation of 1,2-dioxan-3-ols **3** are completely suppressed. This has been also observed in the reaction of alkenes with 1,3-diketones [6].

Scheme 3

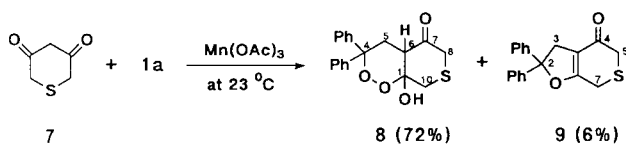


The Reaction of Phosphorus- and Other Sulfur-Containing Active Methylene Compound with 1,1-Diphenylethene (**2a**).

The reaction of dimethoxyphosphinoyl-2-propanone (**1d**) with **2a** in the presence of manganese(III) acetate and oxygen at 40° gave 4-(dimethoxyphosphinoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3da**) and 3-(dimethoxyphosphinoyl)-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**6da**) (Scheme 2, Table 4, entry 27). The ¹H nmr spectrum of **3da** showed that it is a single stereoisomer, but exhibited four peaks with equal heights at δ 3.79-4.03 corresponding to two methoxyl groups. This can be accounted for by the presence of two non-equivalent methoxyl groups, which are located in proximity to the stereocenter at the C-4, and by the spin-spin coupling with P atom (J = 10.8 Hz). Compound **6da**, on the other hand, showed only two peaks for the methoxyl groups. The splitting (J = 12.2 Hz) was presumably caused by the spin-spin coupling with the P atom. Compound **6da** was also obtained in the reaction at 80° in better yield (Table 5, entry 36).

The reaction of tetrahydrothiapyran-3,5-dione (**7**) with **2a** yielded 7-oxo-4,4-diphenyl-2,3-dioxo-9-thiabicyclo-[4.4.0]decan-1-ol (**8**) and 4-oxo-2,2-diphenyl-6-thia-2,3,4,5,6,7-hexahydrobenzo[*b*]furan (**9**) (Scheme 4).

Scheme 4



Structural Assignments.

A -CH₂-CH< unit of **3aa** was shown as an ABX spin system in its ¹H nmr spectrum. The J values were found to be 13.4, 12.1, and 3.2 Hz. The two large J values would suggest that the hydrogen at the C-4 position is axial, that is, the phenylsulfinyl group is equatorial in **3aa**. The ¹³C nmr spectrum of **3aa** exhibited a pair of signals for every carbon, which also indicates the presence of stereoisomers upon the C-3 position: methyl carbons at δ 20.631 and 24.286 (stronger), and methylene carbons at δ 23.659 (stronger) and 27.493. The assignments are based on the

DEPT-135 spectrum. As to the conformation of the hydroxyl group at the C-3 position in the 1,2-dioxan-3-ols, the axial hydroxyl group at the C-3 position would be more stable than the equatorial one due to the anomeric effect [7] in analogous to the case of the 4-carbamoyl-1,2-dioxan-3-ols [4]. As compound **3ab** had a smaller isomer ratio than the others, **3ab** was treated with dimethyl sulfate and potassium carbonate in order to obtain isomeric methyl ethers. It gave two methyl ethers, **10** (44% yield) and **10'** (29% yield) (Figure 1), which could be separated on a silica-gel column chromatography and both showed the presence of an axial hydrogen at the C-4 position in their ¹H nmr spectra as indicated by the large J values (see Experimental). The ¹³C nmr spectra of **10** and **10'** showed their methyl carbon at δ 15.513 and 19.277, respectively. The methyl group of **10** at the C-3 position could be assigned as having an axial position, since an axial methyl signal should appear at higher fields than that of an equatorial methyl group for the steric compression effect [4]. A difference nuclear Overhauser effect experiment showed a slight enhancement (3.4%) in the signals for the methine hydrogen at the C-4 position when the methyl group in **10'** was preirradiated. On the other hand, compound **10** did not show any enhancement. The results indicated that **10'** has an equatorial methyl group which is in a *gauche* conformation with the methine hydrogen at the C-4 position. The conformations of **10** and **10'** are shown in Figure 1.

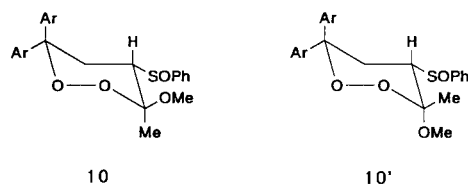


Fig. 1. Ar=4-ClC₆H₄-

Compound **8** has the structure of a bicyclic ring system. The ¹H nmr spectrum (deuteriochloroform, 400 Mz) of **8** showed complicated signals at δ 2.5-2.9 corresponding to two methylene groups and two hydrogens, and a doublet at δ 3.68 corresponding to one hydrogen, besides ten aromatic hydrogens as a multiplet at δ 7.3. The ¹³C nmr and a H,C-COSY spectrum in DMSO-d₆ were taken, and a triplet at δ 2.601 with a large J value (13.9 Hz) could be assigned to the one of the hydrogens at the C-5 position. Thus, the conformation of the hydrogen at the C-6 position could be determined as axial. In order to obtain further information for the conformation of the bicyclic ring system of **8**, MM2 calculations were performed. The relative stabilities of two possible conformations of **8** were found to be 18.4 kcal/mol for the *trans*-fused isomer and 20.8 kcal/mol for the *cis*-fused isomer, indicating that the former is the favored conformation (Figure 2).

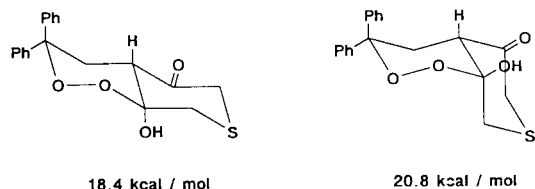


Fig. 2

m-Chloroperbenzoic Acid Oxidation of Sulfoxides to Sulfones.

Although 4-arylsulfonyl-1,2-dioxan-3-ols **3ba-bc** and **3ca** and 3-arylsulfonyl-2-methyl-4,5-dihydrofurans **6ba-bc** and **6ca** were readily obtained in the reactions of arylsulfonyl-2-propanones **1b** and **1c** with **2** and manganese(III) acetate in the presence of oxygen, it should be useful if a sulfoxide was oxidized to a sulfone. Thus, compounds **3aa-ac**, **6aa** and **6ab** were oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to give the corresponding sulfones **3ba-bc**, **6ba** and **6bb**, respectively (Scheme 5 and Table 6).

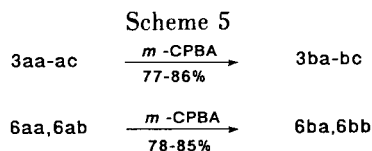


Table 6

Reactions of 4-(Phenylsulfinyl)-1,2-dioxan-3-ols **3** and 3-(Phenylsulfinyl)-4,5-dihydrofurans **6** with *m*-CPBA

Entry	Sulfoxide	Sulfone (yield/%) [a]
37	3aa	3ba (77)
38	3ab	3bb (82)
39	3ac	3bc (86)
40	6aa	6ba (85)
41	6ab	6bb (78)

[a] Isolated yields based on the amount of the substrate used.

In summary, compounds, **3** and **6**, could be obtained in good yields by the thermally controlled reactions employing **1** and **2** in nearly stoichiometric quantities that is in sharp contrast to the reactions of 1,3-diketones [1-3], and acetoacetamides [1,4] in which active methylene compounds were required to be used in large excess. Phenylsulfinyl-2-propanone (**1a**) and arylsulfonyl-2-propanones **1b** and **1c**, and dimethoxyphosphinoyl-2-propanone (**1d**) were less reactive than other β -dicarbonyl compounds, and required slightly higher reaction temperature. *m*-CPBA oxidation of sulfoxides gave the corresponding sulfones in excellent yields.

EXPERIMENTAL

Measurements.

All of the ^1H and ^{13}C nmr spectra were taken with either a JNM PMX-60SI (60 MHz), a JNM EX-90 FT NMR (90 MHz for ^1H and 22.5 MHz for ^{13}C) or JNM GX-400 FT NMR (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometers with tetramethylsilane 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 the data are expressed in cm^{-1} . All melting-points were determined with a Yanaco micromelting point apparatus MP-J3. Mass spectra were measured either on a JMS-DX303HF or a JMS-AX 505W mass spectrometer at an ionizing voltage of 70 eV.

Materials.

Manganese(III) acetate was prepared according to the method in the literature [8]. Phenylsulfinyl-2-propanone (**1a**) was prepared from 2-cyano-2-hydroxypropyl phenyl sulfoxide [9]. β -Keto sulfones **1b** and **1c** were prepared from the reaction of sodium benzenesulfinate or from sodium *p*-toluenesulfinate with chloroacetone in refluxing ethanol [10]. 1,1-Diphenylethenes **2a-e** were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides [6]. Tetrahydrothiapyran-3,5-dione (**7**) was prepared from methyl acetylmercaptoacetate [11]. Dimethoxyphosphinoyl-2-propanone (**1d**), 2-ethyl-1-butene (**2f**) and *m*-CPBA were purchased from Tokyo-Kasei Co. Ltd. and used as received.

Reaction of β -Keto Compounds **1a-d** with Alkenes in the Presence of Manganese(III) Acetate-Oxygen.

The general procedure for the reaction of β -keto compounds with alkenes in the presence of manganese(III) acetate-oxygen was as follows. Manganese(III) acetate (1 mmole) was added to a stirred solution of a mixture of a β -keto compound (1 mmole) and an alkene (1-1.2 mmoles) in acetic acid (25 ml) in a three necked flask equipped with a dry-air inlet tube. The mixture was stirred under a dry-air stream for the period of time and at a temperature shown in Tables 1-4. The reaction was quenched by adding water (60 ml) and the mixture was extracted with benzene. The products were separated on tlc (Wakogel B10) while eluting with a mixture of hexane and ethyl acetate (1:1 v/v). The yields are listed in Tables 1-4. The products were further purified by recrystallization from a mixture of benzene and hexane.

Products.

3-Methyl-4-(phenylsulfinyl)-6,6-diphenyl-1,2-dioxan-3-ol (**3aa**).

This compound had mp 179-180 $^\circ$; ir (potassium bromide): ν max 3200 (-OH), 1309 (>S=O); ^1H nmr (60 MHz, deuteriochloroform): δ 1.73 and 2.08 (3H, s, s, CH_3), 2.28-3.60 (3H, m, $-\text{CH}_2-\text{CH}<$), 4.33 (1H, br s, -OH), 7.53-8.50 (15H, m, 3 x Ph); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ 143.029 (>C=), 142.924 (>C=), 142.193 (>C=), 141.895 (>C=), 140.148 (>C=), 140.299 (>C=), 131.289 (-CH=), 130.814 (-CH=), 130.065 (-CH=), 129.394 (-CH=), 129.215 (-CH=), 128.425 (-CH=), 128.305 (-CH=), 128.171 (-CH=), 128.111 (-CH=), 127.738 (-CH=), 127.619 (-CH=), 127.500 (-CH=), 126.545 (-CH=), 126.381 (-CH=), 126.023 (-CH=), 125.784 (-CH=), 125.352 (-CH=), 124.113 (-CH=), 102.573 (>C<), 99.201 (>C<), 86.805 (>C<), 86.074 (>C<), 66.473 (>CH-), 64.503 (>CH-), 27.493 ($-\text{CH}_2-$), 24.286 (CH_3), 23.659 ($-\text{CH}_2-$), 20.631 (CH_3).

Anal. Calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_4\text{S}$: C, 70.02; H, 5.62. Found: C, 69.93; H, 5.70.

6,6-Bis(4-Chlorophenyl)-3-methyl-4-(phenylsulfinyl)-1,2-dioxan-3-ol (**3ab**).

This compound had mp 177-178°; ir (potassium bromide): ν max 3348 (-OH), 1031 (>S=O); ^1H nmr (60 MHz, deuteriochloroform): δ 1.55 and 1.83 (3H, s, s, CH_3), 2.02-3.32 (3H, m, $-\text{CH}_2-\text{CH}<$), 5.54 (1H, br s, -OH), 6.91-8.06 (13H, m, arom H); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ 144.177 (>C=), 142.492 (>C=), 142.178 (>C=), 141.030 (>C=), 140.970 (>C=), 138.628 (>C=), 134.466 (>C=), 134.068 (>C=), 133.974 (>C=), 133.780 (>C=), 131.333 (-CH=), 131.199 (-CH=), 131.050 (-CH=), 129.499 (-CH=), 129.335 (-CH=), 128.812 (-CH=), 128.604 (-CH=), 128.568 (-CH=), 127.947 (-CH=), 127.723 (-CH=), 127.485 (-CH=), 127.142 (-CH=), 124.263 (-CH=), 124.039 (-CH=), 103.080 (>C<), 99.559 (>C<), 88.789 (>C<), 85.477 (>C<), 64.823 (>CH-), 63.608 (>CH-), 27.418 ($-\text{CH}_2-$), 24.539 (CH_3), 23.674 ($-\text{CH}_2-$), 19.124 (CH_3).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_4\text{Cl}_2\text{S}$: C, 59.62; H, 4.35. Found: C, 59.35; H, 4.37.

6,6-Bis(4-methylphenyl)-3-methyl-4-(phenylsulfinyl)-1,2-dioxan-3-ol (**3ac**).

This compound had mp 146-148°; ir (potassium bromide): ν max 3234 (-OH), 1038 (>S=O); ^1H nmr (60 MHz, deuteriochloroform): δ 1.63 and 2.53 (3H, s, s, CH_3), 2.58-3.42 (3H, m, $-\text{CH}_2-\text{CH}<$), 2.31 (3H, s, CH_3), 2.34 (3H, s, CH_3), 4.17 (1H, br s, -OH), 7.02-8.17 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{25}\text{H}_{26}\text{O}_4\text{S}$: C, 71.06; H, 6.20. Found: C, 71.57; H, 6.38.

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

This compound had mp 163-164°; ir (potassium bromide): ν max 3348 (-OH), 1037 (>S=O); ^1H nmr (60 MHz, deuteriochloroform): δ 1.63 and 1.97 (3H, s, s, CH_3), 1.98-3.47 (3H, m, $-\text{CH}_2-\text{CH}<$), 5.01 (1H, br s, -OH), 6.90-8.00 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_4\text{F}_2\text{S}$: C, 64.17; H, 4.68. Found: C, 63.87; H, 4.55.

6,6-Bis(4-methoxyphenyl)-3-methyl-4-(phenylsulfinyl)-1,2-dioxan-3-ol (**3ae**).

This compound had mp 137-138°; ir (potassium bromide): ν max 3250 (-OH), 1036 (>S=O); ^1H nmr (60 MHz, deuteriochloroform): δ 1.63 and 1.97 (3H, s, s, CH_3), 1.98-4.09 (3H, m, $-\text{CH}_2-\text{CH}<$), 3.67 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.97 (1H, br s, -OH), 6.73-8.02 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{25}\text{H}_{26}\text{O}_6\text{S}$: C, 66.06; H, 5.77. Found: C, 66.08; H, 5.77.

6,6-Diethyl-3-methyl-4-(phenylsulfinyl)-1,2-dioxan-3-ol (**3af**).

This compound had mp 111-112°; ir (potassium bromide): ν max 3296 (-OH), 1023 (>S=O); ^1H nmr (60 MHz, deuteriochloroform): δ 0.41-2.17 (10H, m, 2 x CH_2CH_3), 1.89 and 2.03 (3H, s, s, CH_3), 2.17-3.50 (3H, m, $-\text{CH}_2-\text{CH}<$), 5.18 (1H, br s, -OH), 7.31-8.02 (5H, m, Ph); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ 142.372 (>C=), 141.567 (>C=), 131.050 (-CH=), 130.662 (-CH=), 129.320 (-CH=), 129.081 (-CH=), 124.218 (-CH=), 124.084 (-CH=), 102.351 (>C<), 98.739 (>C<), 84.637 (>C<), 82.732 (>C<), 66.696 (>CH-), 63.936 (>CH-), 28.761 ($-\text{CH}_2-$), 28.537 ($-\text{CH}_2-$), 24.778 ($-\text{CH}_2-$), 24.688 ($-\text{CH}_2-$), 24.465 (CH_3), 24.032 ($-\text{CH}_2-$), 21.019 ($-\text{CH}_2-$), 20.601 (CH_3), 7.503 (CH_3),

7.384 (CH_3), 7.190 (CH_3), 7.056 (CH_3).

Anal. Calcd. for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{S}$: C, 60.38; H, 7.43. Found: C, 60.42; H, 7.33.

3-Methyl-4-(phenylsulfonyl)-6,6-diphenyl-1,2-dioxan-3-ol (**3ba**).

This compound had mp 172-173°; ir (potassium bromide): ν max 3460 (-OH), 1307 and 1148 (> SO_2); ^1H nmr (60 MHz, deuteriochloroform): δ 1.41 and 1.83 (3H, s, s, CH_3), 2.63-3.87 (3H, m, $-\text{CH}_2-\text{CH}<$), 3.94 (1H, br s, -OH), 7.21-8.48 (15H, m, 3 x Ph).

Anal. Calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_5\text{S}$: C, 67.30; H, 5.40. Found: C, 66.79; H, 5.37.

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

This compound had mp 197-198°; ir (potassium bromide): ν max 3376 (-OH), 1303 and 1142 (> SO_2); ^1H nmr (60 MHz, deuteriochloroform): δ 1.63 and 1.90 (3H, s, s, CH_3), 2.67-3.81 (3H, m, $-\text{CH}_2-\text{CH}<$), 3.92 (1H, br s, -OH), 7.27-8.43 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_5\text{Cl}_2\text{S}$: C, 57.63; H, 4.21. Found: C, 57.40; H, 4.13.

6,6-Bis(4-methylphenyl)-3-methyl-4-(phenylsulfonyl)-1,2-dioxan-3-ol (**3bc**).

This compound had mp 185-186°; ir (potassium bromide): ν max 3397 (-OH), 1318 and 1140 (> SO_2); ^1H nmr (60 MHz, deuteriochloroform): δ 1.67 and 1.92 (3H, s, s, CH_3), 2.37 (3H, s, CH_3), 2.45 (3H, s, $-\text{CH}_3$), 2.72-3.83 (3H, m, $-\text{CH}_2-\text{CH}<$), 3.85 (1H, br s, -OH), 7.23-8.47 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{25}\text{H}_{26}\text{O}_5\text{S}$: C, 68.47; H, 5.97. Found: C, 68.52; H, 5.92.

4-(4-Methylphenyl)sulfonyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3ca**).

This compound had mp 189-190°; ir (chloroform): ν max 3578 (-OH), 1318 and 1143 (> SO_2); ^1H nmr (60 MHz, deuteriochloroform): δ 1.77 and 1.93 (3H, s, s, CH_3), 2.60 (3H, s, CH_3), 2.79-3.83 (3H, m, $-\text{CH}_2-\text{CH}<$), 3.88 (1H, br s, -OH), 7.58-8.47 (14H, m, arom H); ^{13}C nmr (22.5 MHz, $\text{DMSO}-d_6$): δ 144.668 (>C=), 144.608 (>C=), 143.206 (>C=), 140.655 (>C=), 140.438 (>C=), 140.342 (>C=), 136.060 (>C=), 135.016 (>C=), 129.780 (-C=), 129.482 (-CH=), 129.407 (-CH=), 128.497 (-CH=), 128.393 (-CH=), 128.333 (-CH=), 127.656 (-CH=), 127.379 (-CH=), 126.110 (-CH=), 125.991 (-CH=), 125.215 (-CH=), 101.670 (>C<), 98.304 (>C<), 86.191 (>C<), 85.460 (>C<), 66.767 (>C<), 65.009 (>CH-), 32.086 ($-\text{CH}_2-$), 30.296 ($-\text{CH}_2-$), 24.210 (CH_3), 21.092 (CH_3), 19.451 (CH_3).

Anal. Calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_5\text{S}$: C, 67.90; H, 5.70. Found: C, 67.77; H, 5.69.

4-(Dimethoxyphosphinoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3da**).

This compound was obtained as a colorless oil; ir (chloroform): ν max 3584 (-OH), 1253 (P=O); ^1H nmr (60 MHz, deuteriochloroform): δ 1.55 (3H, s, CH_3), 2.08-3.59 (3H, m, $-\text{CH}_2-\text{CH}<$), 3.88 (3H, d, J = 10.8 Hz, OCH_3), 3.94 (3H, d, J = 10.8 Hz, OCH_3), 4.23 (1H, br s, OH), 7.03-7.63 (10H, m, 2 x Ph); ^{13}C nmr (22.5 MHz, deuteriochloroform): δ 143.566 (>C=), 140.508 (>C=), 128.529 (-CH=), 128.291 (-CH=), 127.858 (-CH=), 127.395 (-CH=), 126.814 (-CH=), 125.680 (-CH=), 98.441 (>C<), 85.022 (d, J = 12.42 Hz, >C<), 53.636 (d, J = 6.58 Hz, OCH_3), 52.197 (d, J = 6.58 Hz, OCH_3), 39.06 (d, J = 141.68 Hz, >CH-), 30.34 (d, J

= 4.03 Hz, $-\text{CH}_2-$), 25.181 (CH_3); ms: negative ion FAB m/z (relative intensity) 377 ($[\text{M}-1]^-$, 40), 375 (20), 371 (10), 363 (50), 347 (14), 181 (32), 121 (53), 109 (43), 94 (37), 79 (100).

7-Oxo-4,4-diphenyl-2,3-dioxo-9-thiabicyclo[4.4.0]decan-1-ol (**8**).

This compound had mp 156-158°; ir (potassium bromide): ν max 3398 ($-\text{OH}$), 1711 ($> \text{C}=\text{O}$); ^1H nmr (400 MHz, $\text{DMSO}-d_6$): δ 2.527 and 2.862 (AB spin system, 2H, $J_{\text{AB}} = 12.82$ Hz, $-\text{CH}_2-$), 2.601 (1H, t, $J = 13.92$ Hz, $-\text{HCH}-$), 2.735-2.810 (2H, m, $-\text{HCH}-$ and $> \text{CH}-$), 2.739 and 3.709 (AB spin system, 2H, $J_{\text{AB}} = 13.19$ Hz, $-\text{CH}_2-$), 3.434 (1H, s, OH), 7.158-7.568 (10H, m, 2 x Ph); ^{13}C nmr (100 MHz, $\text{DMSO}-d_6$): δ 200.727 ($> \text{C}=\text{O}$), 143.988 ($> \text{C}=\text{O}$), 141.438 ($> \text{C}=\text{O}$), 128.202 ($-\text{CH}=\text{O}$), 128.111 ($-\text{CH}=\text{O}$), 126.563 ($-\text{CH}=\text{O}$), 126.441 ($-\text{CH}=\text{O}$), 125.470 ($-\text{CH}=\text{O}$), 125.409 ($-\text{CH}=\text{O}$), 102.580 ($> \text{C} <$), 86.216 ($> \text{C} <$), 50.516 ($> \text{CH}-$), 35.792 ($-\text{CH}_2-$), 33.606 ($-\text{CH}_2-$), 26.867 ($-\text{CH}_2-$).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{S}$: C, 66.65; H, 5.30. Found: C, 66.63; H, 5.31.

4-Oxo-2,2-diphenyl-6-thia-2,3,4,5,6,7-hexahydrobenzo[*b*]furan (**9**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1640 ($> \text{C}=\text{O}$), 1628 ($\text{C}=\text{C}$); ^1H nmr (60 MHz, deuteriochloroform): δ 3.51 (2H, s, $-\text{CH}_2-$), 3.63 (2H, t, $J = 1.6$ Hz, $-\text{CH}_2-$), 3.68 (2H, t, $J = 1.6$ Hz, $-\text{CH}_2-$), 7.40 (10H, s, 2 x Ph); ^{13}C nmr (22.5 Hz, deuteriochloroform): δ 190.241 ($\text{C}=\text{O}$), 170.282 ($> \text{C}=\text{O}$), 144.012 ($> \text{C}=\text{O}$), 128.469 ($-\text{CH}=\text{O}$), 127.932 ($-\text{CH}=\text{O}$), 125.649 ($-\text{CH}=\text{O}$), 112.164 ($> \text{C}=\text{O}$), 94.895 ($> \text{C} <$), 41.069 ($-\text{CH}_2-$), 33.550 ($-\text{CH}_2-$), 23.451 ($-\text{CH}_2-$).

Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_2\text{S}$: M, 308.0871. Found: m/z 308.0840.

Benzophenone (**4a**).

This compound had mp 48°.

4,4'-Dichlorobenzophenone (**4b**).

This compound had mp 143.3-145.3°.

4,4'-Dimethylbenzophenone (**4c**).

This compound had mp 92-94°.

4,4'-Dimethoxybenzophenone (**4d**).

This compound had mp 140-141°.

4,4'-Difluorobenzophenone (**4e**).

This compound had mp 103-105°.

2,2-Diphenyl-2-hydroxyethyl Acetate (**5a**).

This compound had mp 93-93.5° (lit mp 93-93.5° [2]).

2,2-Bis(4-chlorophenyl)-2-hydroxyethyl Acetate (**5b**).

This compound had mp 95.5-96.2° (lit mp 95.5-96.2° [12]).

2,2-Bis(4-methylphenyl)-2-hydroxyethyl Acetate (**5c**).

This compound had mp 71.0° (lit mp 71.0° [2]).

2,2-Bis(4-fluorophenyl)-2-hydroxyethyl Acetate (**5d**).

This compound had mp 71-72° (lit mp 71-72° [2]).

Reaction of β -Keto Compounds **1a-d** with Alkenes **2a-c** in the Presence of Manganese(III) Acetate at 80°.

To a heated solution of β -keto compound and alkene (1 mmole) in acetic acid (25 ml), the amount of manganese(III) acetate shown in Table 5 was added. The reaction was quenched by adding water (60 ml), the mixture was then extracted with ben-

zene. After removing the benzene, the products were separated either on tlc (Wakogel B10) while eluting with chloroform, or on a silica-gel column eluting with benzene. Yields are listed in Table 5.

2-Methyl-3-(phenylsulfinyl)-5,5-diphenyl-4,5-dihydrofuran (**6aa**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1642 ($\text{C}=\text{C}$), 1018 ($> \text{S}=\text{O}$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.38 (3H, t, $J = 1.6$ Hz, CH_3), 2.86 (1H, dq, $J = 1.6$, 14.4 Hz, $-\text{HCH}-$), and 3.72 (1H, dq, $J = 1.6$, 14.4 Hz, $-\text{HCH}-$), 7.07-7.73 (15H, m, 3 x Ph).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_2\text{S}$: M, 360.1184. Found: m/z 360.1273.

5,5-Bis(4-chlorophenyl)-2-methyl-3-(phenylsulfinyl)-4,5-dihydrofuran (**6ab**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1644 ($\text{C}=\text{C}$), 1111 ($> \text{S}=\text{O}$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.60 (3H, t, $J = 1.6$ Hz, CH_3), 3.07 (1H, dq, $J = 1.6$, 14.4 Hz, $-\text{HCH}-$), and 4.00 (1H, dq, $J = 1.6$, 14.4 Hz, $-\text{HCH}-$), 7.67-8.33 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_2\text{Cl}_2\text{S}$: M, 428.0405. Found: m/z 428.0422.

2-Methyl-3-(phenylsulfonyl)-5,5-diphenyl-4,5-dihydrofuran (**6ba**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1640 ($\text{C}=\text{C}$), 1319 and 1146 ($> \text{SO}_2$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.67 (3H, t, $J = 1.8$ Hz, CH_3), 3.95 (2H, q, $J = 1.8$ Hz, $-\text{CH}_2-$), 7.81-8.77 (15H, m, 3 x Ph).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_3\text{S}$: M, 376.1133. Found: m/z 376.1154.

5,5-Bis(4-chlorophenyl)-2-methyl-3-(phenylsulfonyl)-4,5-dihydrofuran (**6bb**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1640 ($\text{C}=\text{C}$), 1320 and 1147 ($> \text{SO}_2$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.67 (3H, t, $J = 1.8$ Hz, CH_3), 3.88 (2H, q, $J = 1.8$ Hz, $-\text{CH}_2-$), 7.77-8.77 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}_3\text{Cl}_2\text{S}$: M, 444.0354. Found: m/z 444.0412.

5,5-Bis(4-methylphenyl)-2-methyl-4-(phenylsulfonyl)-4,5-dihydrofuran (**6bc**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1640 ($\text{C}=\text{C}$), 1321 and 1144 ($> \text{SO}_2$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.53 (6H, s, 2 x CH_3), 2.70 (3H, t, $J = 1.8$ Hz, CH_3), 3.88 (2H, q, $J = 1.8$ Hz, $-\text{CH}_2-$), 7.57-8.67 (13H, m, arom H).

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}$: M, 404.1446. Found: m/z 404.1444.

3-(4-Methylphenyl)sulfonyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**6ca**).

This compound was obtained as a pale yellow oil; ir (chloroform): ν max 1641 ($\text{C}=\text{C}$), 1318 and 1145 ($> \text{SO}_2$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.67 (3H, s, CH_3), 2.71 (3H, t, $J = 1.8$ Hz, CH_3), 3.97 (2H, q, $J = 1.8$ Hz, $-\text{CH}_2-$), 7.80-8.67 (14H, m, arom H).

Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_3\text{S}$: M, 390.1290. Found: m/z 390.1313.

3-(Dimethoxyphosphinoyl)-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**6da**).

This compound was obtained as a colorless oil; ir (chloroform): ν max 1642 ($\text{C}=\text{C}$), 1231 ($\text{P}=\text{O}$); ^1H nmr (60 MHz, deuteriochloroform): δ 2.57 (3H, q, $J = 1.6$ Hz, CH_3), 3.73-4.10 (2H, m,

-CH₂-), 4.01 (6H, d, J = 12.2 Hz, 2 x OCH₃), 7.83-8.27 (10H, m, 2 x Ph).

Anal. Calcd. for C₁₉H₂₁O₄P: M, 344.1177. Found: m/z 344.1178.

Oxidations of 4-(Phenylsulfinyl)-1,2-dioxan-3-ols (**3aa-ac**) and 3-(Phenylsulfinyl)-4,5-dihydrofurans (**6aa** and **6ab**) with *m*-CPBA.

A solution of *m*-CPBA (1 mmole) in dichloromethane (20 ml) was added dropwise to a stirred solution of **3** or **6** (1 mmole) in dichloromethane (20 ml) at room temperature and the reaction mixture was stirred under reflux for 20 minutes. The solution was washed with aqueous sodium carbonate solution and dried over magnesium sulfate. After removing the solvent, the resulting products were separated on tlc (Wakogel B10) while eluting with chloroform. Yields are listed in Table 6.

Methylation of 6,6-Bis(4-chlorophenyl)-3-methyl-4-(phenylsulfinyl)-1,2-dioxan-3-ol (**3ab**).

Anhydrous potassium carbonate (180 mg) and dimethyl sulfate (200 mg) were added to **3ab** (463 mg) in anhydrous acetone (10 ml). The mixture was heated under reflux for 8 hours. After water (8 ml) was added, the mixture was stirred at room temperature for 6 hours and then the acetone was removed. The residue was extracted with chloroform (total 60 ml) and the extract was dried over anhydrous sodium sulfate. After removing the chloroform, the crude product was chromatographed on a silica-gel column eluting with a mixture of ether and hexane (1:1 v/v) to give 6,6-bis(4-chlorophenyl)-*r*-3-methoxy-3-methyl-*t*-4-(phenylsulfinyl)-1,2-dioxane (**10**) (212 mg, 44% yield), and 6,6-bis(4-chlorophenyl)-*r*-3-methoxy-3-methyl-*c*-4-(phenylsulfinyl)-1,2-dioxane (**10'**) (136 mg, 29% yield).

6,6-Bis(4-chlorophenyl)-*r*-3-methoxy-3-methyl-*t*-4-(phenylsulfinyl)-1,2-dioxane (**10**).

This compound had mp 150-151° (from benzene-hexane); ir (potassium bromide): ν max 1043 (>S=O); ¹H nmr (400 MHz, deuteriochloroform): δ 1.718 (3H, s, CH₃), 2.418 (1H, dd, J = 13.19, 13.92 Hz, -HCH-), 2.56 (1H, d, J = 13.19 Hz, -HCH-), 2.84 (1H, d, J = 13.92 Hz, >CH-), 3.44 (3H, s, OCH₃), 6.59-7.65 (13H, m, arom H); ¹³C nmr (22.5 MHz, deuteriochloroform): δ 143.047 (>C=), 142.410 (>C=), 138.099 (>C=), 134.031 (>C=), 133.515 (>CH=), 130.965 (-CH=), 129.265 (-CH=), 128.536 (d, -CH=), 127.565 (-CH=), 126.927 (-CH=), 124.165 (-CH=), 106.284 (>C<), 86.855 (>C<), 66.848 (>CH-), 50.030 (OCH₃), 26.928 (-CH₂-), 15.513 (CH₃).

Anal. Calcd. for C₂₄H₂₂O₄Cl₂S: C, 60.38; H, 4.65. Found: C, 60.30; H, 4.71.

6,6-Bis(4-chlorophenyl)-*r*-3-methoxy-3-methyl-*c*-4-(phenylsulfinyl)-1,2-dioxane (**10'**).

This compound had mp 197-198°; ir (chloroform): ν max 1056 (>S=O); ¹H nmr (400 MHz, deuteriochloroform): δ 1.453 (3H, s, CH₃), 2.418 (1H, dd, J = 4.03, 12.48 Hz, -HCH-), 2.537 (1H, dd, J = 12.48, 13.92 Hz, >CH-), 2.994 (1H, dd, J = 4.03, 13.92 Hz, -HCH-), 3.560 (3H, s, OCH₃), 6.93-7.56 (13H, m, arom H); ¹³C nmr (22.5 MHz, deuteriochloroform): δ 142.987 (>C=), 141.013 (>C=), 138.676 (>C=), 134.426 (>C=), 133.697 (>C=), 131.025 (-CH=), 129.295 (-CH=), 128.718 (-CH=), 128.445 (-CH=), 128.111 (-CH=), 127.868 (-CH=), 124.590 (-CH=), 102.094 (>C<), 85.731 (>C<), 65.786 (>CH-), 49.544 (OCH₃), 24.135 (-CH₂-), 19.277 (CH₃).

Anal. Calcd. for C₂₄H₂₂O₄Cl₂S: C, 60.38; H, 4.65. Found: C, 60.57; H, 4.65.

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