Manganese-(II) and (III)-mediated Free-radical Cyclisation of Alkenes, β-Keto Esters and Molecular Oxygen

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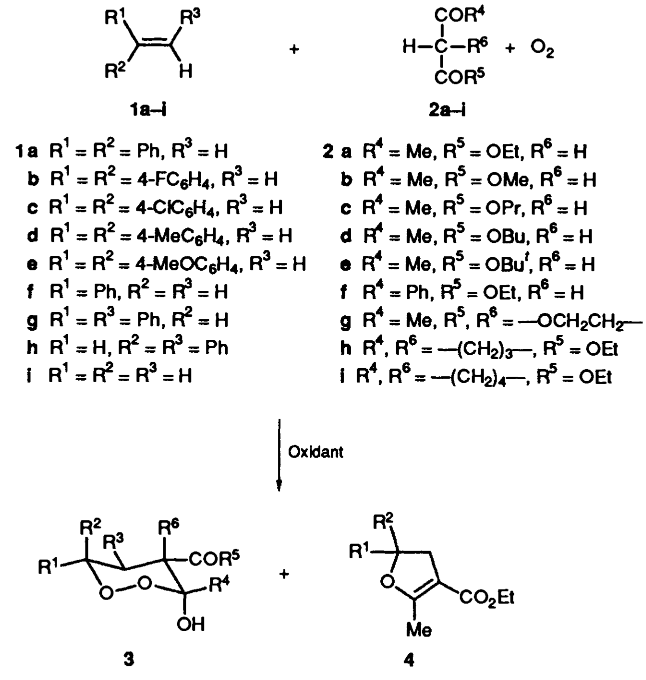
The reactions of substituted ethenes with β-keto esters in the presence of a mixture of manganese(II) and manganese(III) acetates, and molecular oxygen yielded substituted 1,2-dioxan-3-ols **3** in 14–95% yields. Cobalt(III) acetate, potassium permanganate, lead(IV) acetate, copper(II) acetate, chromium(VI) trioxide, thallium(III) acetate, ammonium cerium(IV) nitrate and iron(III) perchlorate were also used in place of manganese(III) acetate. Effects on the product yields of substituents in the alkenes and β-keto esters have been examined and reaction mechanisms are discussed.

We recently reported that manganese(II) or manganese(III) acetate-mediated free-radical cyclisation of alkenes with 1,3-diones [1] or acetoacetamides,[2] and molecular oxygen yielded 1,2-dioxan-3-ols **3** in good yields. It was found that the reaction of alkenes with acetoacetamide and oxygen in the presence of manganese(III) acetate gave compounds **3** most effectively. Manganese(II) acetate, on the other hand, gave better yields for the reaction of alkenes and 1,3-diketones having active methine and oxygen, but not for active methylene compounds which were best transformed into compounds **3** with manganese(III) acetate.[1b,c] We have further examined the reaction of alkenes with β-keto esters and oxygen in the presence of various transition-metal salts with particular attention to the role of manganese(III) acetate, and the results are described in this paper.



Scheme 1

Results and Discussion

Reactions of 1,1-*Diphenylethene* **1a** *with Ethyl 3-Oxobutanoate* **2a** *and Oxygen in the Presence of Various Metal Salts or Oxide.*—Reaction of 1,1-diphenylethene **1a** with ethyl 3-oxobutanoate **2a** in the presence of manganese(II) acetate under a dry air stream gave ethyl *cis*-3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate **3aa** (Scheme 1; Table 1, entry 1). The structural assignment was based on the ^{1}H NMR, ^{13}C NMR and IR spectra, and elemental analysis, as well as on the compound's similarity to 4-acetyl-3-methyl-1,2-dioxan-3-ol. The structure of the latter was confirmed by X-ray crystallography.[1a,b] The yield was improved up to 68–72% either by performing the reaction for longer reaction time (entry 2) or at an elevated temperature (entry 3). However, either ethyl 2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate **4aa** or benzophenone **5a** was formed as a by-product. The reaction under a stream of oxygen also yielded **5a** and 2,2-diphenyl-2-hydroxyethyl acetate **6a** as minor products (Fig. 1; entry 4). By carrying out the reaction using a small amount of manganese(III) acetate at a 1 : 3 : 0.1 molar ratio for **1a** : **2a** : $Mn^{III}(OAc)_3$ under a dry air stream, only **3aa** was obtained in a comparable yield (65%), other by-products not being formed, although one-third of the unchanged alkene was recovered (entry 5). In the reaction at a molar ratio of 1 : 3 : 1 for **1a** : **2a** : $Mn^{III}(OAc)_3$ the products again consisted of **3aa** and **4aa** (entry 8). Thus, it seemed that the reaction using a mixture of $Mn^{II}(OAc)_2$ and a small amount of $Mn^{III}(OAc)_3$ at a lower temperature could be a better reagent for the formation of 1,2-dioxan-3-ols *via* the alkene–β-keto ester–oxygen intermolecular cyclisation. Before investigating the reaction further in detail, other metal salts were examined. Copper(II), nickel(II) and thallium(III) acetates were not reactive. Chromium(VI) trioxide and cobalt(III) acetate were reactive, but not effective for the formation of **3aa** (entries 11 and 12). The reactions of potassium permanganate, and ammonium cerium nitrate (CAN) in acetic acid and acetonitrile gave **3aa** in rather unsatisfactory yields (entries 10, 13 and 14). The reaction of **1a** with **2a** in the presence of iron(III) perchlorate in acetic acid yielded **4aa**, **5a** and ethyl 2-methyl-5-phenylfuran-3-carboxylate **7** (entry 15).

Reactions using a combination of manganese(II) acetate and various oxidizing reagents under a current of dry air at 23 °C (Table 2) were then investigated. The reaction of **1a** and **2a** with a 1 : 0.1 molar mixture of manganese(II) and manganese(III) acetates gave the maximum yield for **3aa** (95%, entry 17). Manganese(II)–cobalt(III) acetates yielded similar result (entry 18). Potassium permanganate, chromium(VI) trioxide, thallium(III) acetate, and CAN in combination with manganese(II) acetate also proved to be excellent reagents (entries 19, 22, 23 and 24). Thus, the combination of a 1 : 0.1 molar mixture of manganese(II)–manganese(III) acetates was chosen for further investigation since it gave the best yield for the 1,2-dioxan-3-ol.

Reactions with Various Alkenes.—The reactions were exam-

Table 1 Reaction of 1,1-diphenylethene **1a** with ethyl 3-oxobutanoate **2a** in the presence of a metal salt or oxide–O_2[a]

Entry	Metal salt or oxide	Molar ratio[b]	Solvent	Temp. (°C)	Time (h)	Product composition (yield/%)[c] 1a	3aa	4aa	5a	6a	7
1	$Mn(OAc)_2$[d]	1:3:1	AcOH	23	24	71	8				
2	$Mn(OAc)_2$[d]	1:3:1	AcOH	23	96		72		7		
3	$Mn(OAc)_2$[d]	1:3:1	AcOH	60	24		68	18			
4	$Mn(OAc)_2$[e]	1:3:1	AcOH	60	24	20	39		15	11	
5	$Mn(OAc)_3$	1:3:0.1	AcOH	23	24	33	65				
6	$Mn(OAc)_3$	1:1:1	AcOH	23	12		43	15		17	
7	$Mn(OAc)_3$	1:2:1	AcOH	23	12		54	22			
8	$Mn(OAc)_3$	1:3:1	AcOH	23	12		74	14			
9	$Mn(OAc)_3$[e]	1:3:1	AcOH	23	24				39	40	
10	$KMnO_4$	1:3:1	AcOH	23	3		42	9	12	15	
11	CrO_3	1:3:1	AcOH	23	5	18			44	14	
12	$Co(OAc)_3$	1:3:1	AcOH	23	24	46			23	18	
13	$(NH_4)_2Ce(NO_3)_6$	1:3:1	AcOH	23	24		51	28			
14	$(NH_4)_2Ce(NO_3)_6$	1:3:1	MeCN	23		25	13	44			
15	$Fe(ClO_4)_3$	1:3:1	AcOH	23		21		13	16		6
16	$Fe(ClO_4)_3$	1:3:1	MeCN	23		12		53			

[a] The reactions were carried out with exposure to the atmosphere unless otherwise stated. [b] **1a**:**2a**:metal salt or oxide. [c] Isolated yield based on **1a** used. [d] Under a dry air stream. [e] Under an oxygen atmosphere.

Table 2 Reaction of 1,1-diphenylethene **1a** with ethyl 3-oxobutanoate **2a** in the presence of a mixture of $Mn(OAc)_2$ and an oxidant, and O_2[a]

Entry	Oxidant	Molar ratio[b]	Time (h)	Product composition (yield/%)[c] 1a	3aa	4aa	6a
17	$Mn(OAc)_3$	1:3:1:0.1	12		95	3	
18	$Co(OAc)_3$	1:3:1:0.1	12		93		
19	$KMnO_4$[d]	1:3:1:0.1	1.5		79	9	
20	$Pb(OAc)_4$	1:3:1:0.1	12		32	32	20
21	$Cu(OAc)_2$	1:3:1:0.1	12	58	35		
22	CrO_3[d]	1:3:1:0.1	3		80	10	
23	$Tl(OAc)_3$	1:3:1:0.1	12	5	73		
24	$(NH_4)_2Ce(NO_3)_6$	1:3:1:0.1	12		62	24	
25	$Fe(ClO_4)_3$	1:3:1:0.6	12	68	24		

[a] The reactions were carried out in acetic acid at 23 °C under a dry air stream. [b] **1a**:**2a**:$Mn(OAc)_2$:Oxidant. [c] Isolated yield based on **1a** used. [d] **1a** and **2a** were added to the mixture 10 min after the $Mn(OAc)_2$ and oxidant had been mixed.

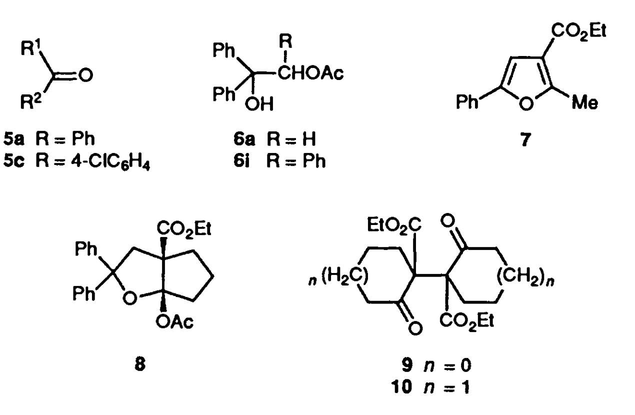


Fig. 1

ined for 1,1-bis(4-fluorophenyl)ethene **1b**, 1,1-bis(4-chlorophenyl)ethene **1c**, 1,1-bis(4-methylphenyl)ethene **1d**, 1,1-bis(4-methoxyphenyl)ethene **1e**, styrene **1f**, (*Z*)-1,2-diphenylethene **1g** and (*E*)-1,2-diphenylethene **1h**, and 1,1,2-triphenylethene **1i** (Table 3, entries 26–33). The reactions with 1,1-diaryl substituted ethenes **1b–e** and styrene **1f** gave good yields for the corresponding ethyl 3-hydroxy-3-methyl-1,2-dioxane-4-carboxylates **3ba–fa**, but 1,2-disubstituted alkenes, such as (*Z*)-1,2-diphenylethene **1g** and (*E*)-1,2-diphenylethene **1h**, gave the products in poor yields. Compounds **1g** and **1h** both gave the same 1,2-dioxan-3-ol **3ga**. 1,1,2-Triphenylethene **1i** gave **5a** and 2-hydroxy-1,2,2-triphenylethyl acetate **6i**. 2-Ethylbut-1-ene, oct-1-ene and cyclohexene gave a mixture of undefined compounds. Thus, it seems that the reaction is limited to phenyl substituted ethenes.

Reactions with Various β-Keto Esters.—The reactions were examined for methyl 3-oxobutanoate **2b**, propyl 3-oxobutanoate **2c**, butyl 3-oxobutanoate **2d**, *tert*-butyl 3-oxobutanoate **2e**, ethyl benzoylacetate **2f**, 2-acetylbutyrolactone **2g**, ethyl 2-oxocyclopentanecarboxylate **2h** and ethyl 2-oxocyclohexanecarboxylate **2i** with **1a**. The results are summarized in Table 3 (entries 34–41). In the reaction of **2h**, an acetate **8** and a dimeric compound **9** were obtained along with **3ah** (Fig. 1). The structure of **8** can be assigned as *cis*-fused 1-acetoxy-5-ethoxycarbonyl-3,3-diphenyl-2-oxabicyclo[3.3.0]octane **8** since a *trans*-fused bicyclo[3.3.0] system would be highly strained.

Structural Assignments.—In contrast to the reaction of acetoacetamides,[2] which gave an equilibrium mixture of two stereoisomers, the reactions of β-keto esters yielded a single stereoisomer. The ^1H NMR spectrum of **3aa** showed the presence of an ethoxy group at δ 1.27 (3 H, t, J 7.0 Hz) and 4.17 (2 H, q, J 7.0 Hz), a methyl group at δ 1.38 (3 H, s), a $-CH_2-CH<$ unit at δ 2.83 (3 H, m), and two phenyl groups at δ 7.2–7.5 (10 H, m). The CH_2CH unit in **3aa** was shown as an ABX spin system (δ_A 4.09, δ_B 4.87, δ_X 5.55, J_{AB} 12.3, J_{AX}

Table 3 Reactions of 1,1-disubstituted ethenes **1** with β-keto esters **2** in the presence of $Mn(OAc)_2$–$Mn(OAc)_3$ and O_2 [a]

Entry	Ethene	β-Keto ester	Production composition [yield(%)] [b]
26	**1b**	**2a**	**3ba** [76] **4ba** [9]
27	**1c**	**2a**	**3ca** [91] **5c** [9]
28	**1d**	**2a**	**3da** [81] **4da** [10]
29	**1e**	**2a**	**3ea** [91] **4ea** [9]
30	**1f**	**2a**	**3fa** [61] **4fa** [5]
31	**1g**	**2a**	**1g** [71] **3ga** [14]
32	**1h**	**2a**	**1h** [33] **3ga** [28]
33	**1i**	**2a**	**1i** [33] **5a** [15] **6i** [31]
34	**1a**	**2b**	**3ab** [90]
35	**1a**	**2c**	**3ac** [83]
36	**1a**	**2d**	**3ad** [81]
37	**1a**	**2e**	**3ae** [65]
38	**1a**	**2f**	**3af** [68]
39	**1a**	**2g**	**3ag** [85]
40	**1a**	**2h**	**3ah** [72] **8** [14] **9** [27] [c]
41	**1a**	**2i**	**3ai** [27] **5a** [17] **6a** [52] **10** [19] [c]

[a] The reactions were carried out in acetic acid at a molar ratio of 1:2:$Mn(OAc)_2$:$Mn(OAc)_3$ = 1:3:1:0.1 for 12 h at 23 °C under a dry-air stream. [b] Isolated yield based on **1** used. [c] Isolated yield based on **2** used.

3aa

3ag

3ai

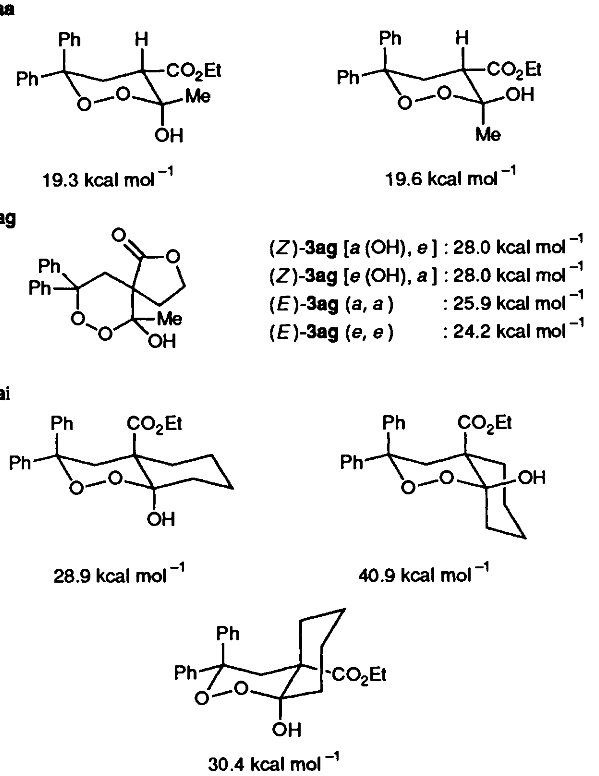


Fig. 2 MM2 calculation of **3aa**, **3ag** and **3ai**

12.3 and J_{BX} 3.9 Hz) when the spectrum was taken with the aid of a shift reagent, [Eu(fod)$_3$]. The two large coupling constants (J_{AB} = J_{AX} 12.3 Hz) indicated that a hydrogen at the 4-C position had an axial conformation (Fig. 2). The configuration at the 3-C was determined on the basis of MM2 calculations. The calculations were performed only on their chair conformations and it was found that (*Z*)-**3aa** [OH(*a*), CO_2Et(*e*)] had a lower energy (19.3 kcal mol^{-1}) than (*E*)-**3aa** [OH(*e*), CO_2Et(*e*); 19.6 kcal mol^{-1}]. The lower energy of (*Z*)-**3aa**, which has an axial hydroxy group, could be ascribed to an anomeric effect.[3] MM2 calculations were also carried out for **3ag** and **3ai** in order to determine the relative stabilities of the possible conformations. The results indicated that among possible four stereostructures for **3ag**, (*E*)-**3ag** (*e,e*) possesses a lower energy than others. By inspection of a computer-drawn picture of (*E*)-**3ag** (*e,e*), it was shown that (*E*)-**3ag** (*e,e*) has a 'twist boat' form for the 1,2-dioxane ring, probably because of the presence of the neighbouring butyrolactone ring. It was also shown that a *trans*-fused bicyclo[4.4.0] ring for **3ai** is more stable than a *cis*-fused one.

Although compound **3aa** is a single stereoisomer, treatment of **3aa** with camphor-10-sulfonic acid in methanol gave a mixture of two isomeric methyl ethers **11aa** and **11aa'**, which could not be separated into individual isomers on a silica gel plate. The ^1H NMR spectrum (60 MHz; $CDCl_3$) of the mixture showed two singlets for methyl groups at the 3-C position at δ 1.37 for **11aa** (major component) and δ 1.30 for **11aa'** (minor component) with intensities being 3.2:1. The ^{13}C NMR spectrum (22.5 MHz; $CDCl_3$) indicated the presence of the methyl group at the 3-C position and the methylene carbon (5-C), which resonated at δ 14.14 and 31.15 for **11aa**, and δ 15.53 and 34.37 for **11aa'**. These spectral data indicate that the methyl group at the 3-C position in **11aa** is axial, and that in **11aa'** is equatorial (Fig. 3). The assignments were based on the steric compression effect between the methyl group and the methylene (5-C) as has been observed in the case of 4-carbamoyl-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxanes;[2] compared with the equatorial methyl group, the axial 3-methyl group resonated at a slightly lower field in the ^1H NMR spectrum and at a slightly higher field in ^{13}C NMR spectrum. An upfield shift of the methylene carbon in **11aa** is in harmony with the presence of the axial methyl group at the 3-C position.

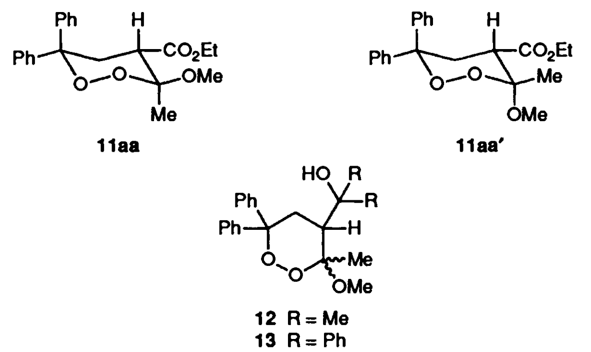
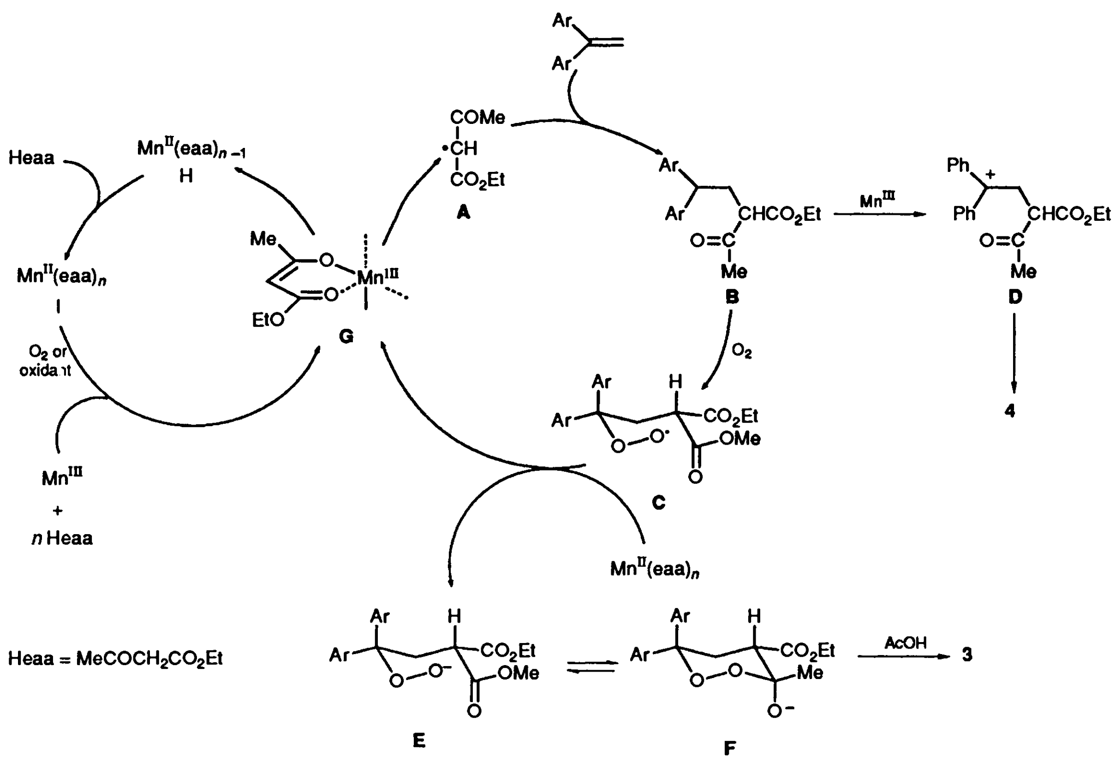


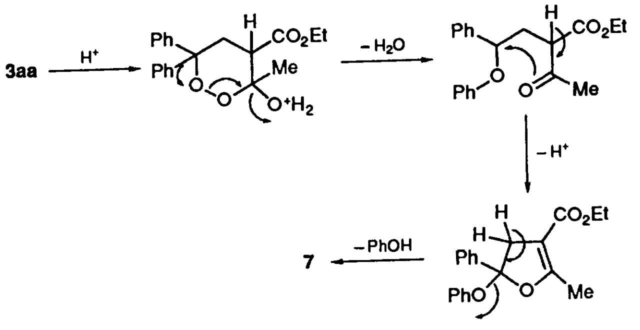
Fig. 3

Reaction of Ethyl 3-Methoxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylates **11aa** *and* **11aa'**.—In order to examine whether the 1,2-dioxane ring is stable or not towards the nucleophilic reagent, the reactions of the methyl ethers **11aa** and **11aa'** with methyl- and phenyl-magnesium halides were carried out. The reactions yielded 4-(1-hydroxy-1-methylethyl)-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane **12** and 4-(hydroxydiphenylmethyl)-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane **13**, respectively. It was thus demonstrated that the carbonyl group at the 4-C position can be converted into other functional groups without a change in the 1,2-dioxane ring system.

Reaction Mechanisms.—The reaction may be accounted for in terms of radical reactions initiated by 1-ethoxycarbonyl-2-oxopropyl radicals **A**, ·CH(COMe)CO_2Et, formed by the interaction of manganese(III) acetate and ethyl 3-oxobutanoate **2a** (Scheme 2). We attempted unsuccessfully to purify a TLC fraction which, showing the presence of several ethoxy groups in



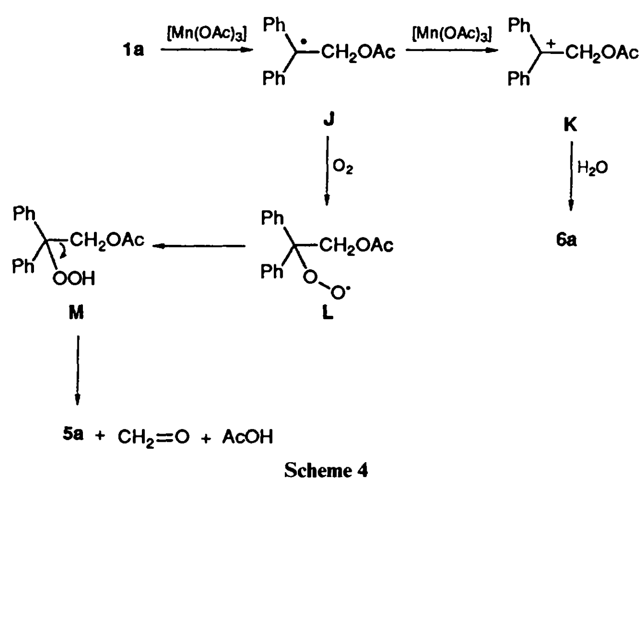
Scheme 2



Scheme 3

its ^{1}H NMR spectrum, we thought might contain a dimeric compound of **2a**. Nevertheless, formation of radicals **A** is supported by the formation of dimeric compounds **9** and **10** in the reactions of ethyl 2-oxocyclopentanecarboxylate **2h** and ethyl 2-oxocyclohexanecarboxylate **2i**, respectively. Reaction of radicals **A** with an alkene gives stable carbon radicals **B**, which either trap oxygen to form peroxyl radicals **C** or are oxidized to the corresponding cations **D**. Under the reaction conditions described, that is, in a dry air stream and at room temperature, the former path should be favoured. Reduction with Mn^{II} of the peroxyl radicals **C** would give the peroxyl anions **E** which would then equilibrate with the cyclized alkoxyl anions **F**. The latter, abstracting a proton from solvent, would give **3aa**. However, the path **B**→**D** became competitive for reactions both at an elevated temperature and for those with a higher concentration of manganese(III) acetate; the carbocations **D** cyclize and are deprotonated to yield **4aa**. Manganese(II) acetate, manganese(III) acetate, potassium permanganate and CAN are able to produce **3aa** when they are used alone as shown in Table 1. Cobalt(III) acetate reacted with an alkene to yield **5a** and **6a**. This could be accounted for in terms of the higher redox potential[4] and more inert nature of cobalt(III) acetate compared with manganese(III) acetate. Iron(III) perchlorate reacted with **2a** and **1a** to yield **4aa** and **7**, but did not give **3aa**. However, it seems that **3aa** can be converted into **7** under acid conditions and a similar conversion has been observed in the acid-catalysed reaction of 4-acetyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol.[1c] In fact, treatment of **3aa** with perchloric acid gave **7** in quantitative yield. A plausible mechanism is shown in Scheme 3.

We described in a previous paper how compounds **5a** could be derived from **6a**. However, when the reactions were carried out under an atmosphere of oxygen (Table 1, entries 4 and 9), the yields of **5a** increased markedly. Electron transfer processes account for the formation of **6a**.[5,6] To account for the formation of **5a**, on the other hand, it is reasonable to assume that the radical intermediates **J**, formed by the reaction of **1a** with manganese(III) acetate, would also react with oxygen to give peroxyl radicals **L**. The latter upon decomposition *via* a hydroperoxide **M** would yield **5a**, acetic acid and formaldehyde (detected as its 2,4-DNP; Scheme 4). In harmony with our view the reaction of 2-hydroxy-2,2-diphenylethyl acetate **6a** with



Scheme 4

manganese(III) acetate at 23 °C failed to give **5a**, unchanged **6a** being recovered.

As has been shown in Table 2, the combination of manganese(II) and manganese(III) acetates is a far more effective reagent for 1,2-dioxan-3-ol formation than either separately: thus manganese(II) acetate itself can give **3aa** in better yield at room temperature, but takes longer whilst manganese(III) acetate tends to give a mixture of **3aa** and **4aa**. Manganese(II) acetate itself could not be oxidized to manganese(III) acetate by oxygen alone, but when oxygen was bubbled through an acetic acid solution of manganese(II) acetate containing ethyl 3-oxobutanoate **2a**, the solution turned brown in 7 h and showed its λ_{max} at 447 nm, which is the same as manganese(III) acetate in acetic acid.[7] The solution then turned colourless at room temperature after several hours and gave a white precipitate, which was found to be anhydrous manganese(II) acetate. It is known that bis(pentane-2,4-dionato)manganese(II) is unstable towards oxygen, particularly in solution, and tends to be oxidized to tris(pentane-2,4-dionato)manganese(III) even at room temperature.[8] This suggests that **2a** plays an important role in transforming manganese(II) to manganese(III) species during aerobic oxidation. The role of the other oxidant used in the reaction should also be to oxidize Mn^{II} ions to Mn^{III}. Thus, the Mn^{III} complex was formed from Mn^{II} either by the reaction with another oxidant molecule or oxygen and then an ethyl acetoacetate (abbreviated Heaa)-coordinated Mn^{III} complex, for which a formula of $Mn^{III}(eaa)_n$ **G** was tentatively assigned, would decompose to produce the radicals **A**. The reduced $Mn^{II}(eaa)_{n-1}$ **H** would then give back $Mn^{II}(eaa)_n$ **I**, thus being recycled.

The fact that the Mn^{III} complex is a labile one,[9] must be also responsible for the ease of formation of the radicals **A**; acetate ion, axially coordinated to the Mn^{III} ions, could be exchanged quickly with ethyl acetoacetate, which then splits off from Mn^{II} as radical **A** after being oxidized. Iron(III) perchlorate and CAN also showed a similar tendency, but since the cobalt(III) complex would be a stable species at room temperature it would not produce radicals **A** in the reaction. Contrary to our expectations, the reaction of **1a** and **2a** in the presence of Mn^{II} or Mn^{III} under a pure oxygen atmosphere gave either only a poor or no yield of **3aa**, although the yield of **5a** increased. Since a large quantity of complex products was formed, which had no aromatic hydrogen in its ^{1}H NMR spectrum, it seems to be likely that there is some reaction between radicals **A** and oxygen.

It seems possible that the radicals **A** staying in the proximity of the Mn^{III} ion react successively with alkene and oxygen which are coordinated to the Mn^{III} ion in a manner similar to Snider's mechanism for the reaction of α,α′-dicarbonylmethyl radicals with alkene.[10]

Conclusions.—Manganese(II and III)-mediated reaction of alkenes, β-keto esters and O_2 give 1,2-dioxan-3-ols in excellent yields. Whilst 1,1-diarylethenes always give good yields, 1,2-diarylethenes are less reactive. Alkenes having no phenyl substituent give no 1,2-dioxan-3-ols. Both acyclic and cyclic β-keto esters gave 1,2-dioxan-3-ols.

Experimental

Measurements.—All of the ^{1}H and ^{13}C spectra were taken with a JNM PMX-60SI (60 MHz) and a JNM EX-90 FT NMR (90 MHz for ^{1}H and 22.5 MHz for ^{13}C) spectrometer with tetramethylsilane being used as the internal standard. Chemical shifts are shown as δ values and J values are in Hz. The IR spectra were measured on a JASCO A-102 IR spectrometer and the values are expressed in cm^{-1}. Mass spectra were measured on a JMS-DX303HF spectrometer at an ionizing voltage of 70 eV. All of the melting-points were determined with a Yanaco micromelting-point apparatus MP-J3.

Materials.—Manganese(III) acetate dihydrate[11] was prepared according to a method described in literature. 1,1-Diphenylethenes **1a–e** and 1,1,2-triphenylethene **1i** were prepared by dehydration of the corresponding alcohols which were synthesised from substituted acetophenones or benzophenone and arylmagnesium bromides.[12] Styrene **1f** (Wako), (*Z*)-1,2-diphenylethene **1g** (Aldrich), (*E*)-1,2-diphenylethene **1h** (Katayama), and β-keto esters **2a–i** (Wako and Tokyo-Kasei) were purchased and used as received.

Reaction of 1,1-*Diphenylethene* **1a** *with Ethyl* 3-*Oxobutanoate* **2a** *in the Presence of a Metal Salt or an Oxide–Molecular Oxygen.*—The general procedure for the reaction of 1,1-diphenylethene **1a** with ethyl 3-oxobutanoate **2a** in the presence of a metal salt or oxide and oxygen was as follows. A metal salt (0.1–1 mmol) was added to a stirred solution of **1a** (1 mmol) and **2a** (3 mmol) in acetic acid (25 cm^3) in a three-necked flask equipped with a dry-air inlet tube. The mixture was stirred at 23 °C for the period of time shown in Table 1. The solvent was removed under reduced pressure and residue was triturated with sulfuric acid (1 mol dm^{-3}, 30 cm^3), and then extracted with chloroform. The products were separated on TLC (Wakogel B10) with chloroform as the eluent. The products were further purified by recrystallization. Yields are listed in Table 1.

Ethyl cis-3-*hydroxy*-3-*methyl*-6,6-*diphenyl*-1,2-*dioxane*-4-*carboxylate* **3aa**. M.p. 151 °C (from ethanol) (Found: C, 70.1; H, 6.4. Calc. for $C_{20}H_{22}O_5$: 70.16; H, 6.48%); $\nu_{max}(CHCl_3)$/cm^{-1} 3604 (OH) and 1729 (C=O); δ_H(90 MHz; $CDCl_3$; Me_4Si) 1.27 (3 H, t, J 7.0, CH_2CH_3), 1.38 (3 H, s, Me), 2.83 (3 H, m, CH_2CH), 3.50–4.10 (1 H, br s, OH), 4.17 (2 H, q, J 7.0, OCH_2CH_3) and 7.20–7.50 (10 H, m, 2 × Ph); δ_C(22.5 MHz; $CDCl_3$; Me_4Si) 171.49 (C=O), 143.22 (>C=), 140.77 (>C=), 128.44 (=CH–), 128.29 (=CH–), 127.91 (=CH–), 127.32 (=CH–), 126.71 (=CH–), 125.74 (=CH–), 98.50 (3-C), 85.12 (6-C), 61.23 (OCH_2CH_3), 45.45 (4-C), 31.71 (5-C), 24.42 (Me) and 14.08 (CH_2CH_3).

Ethyl 2-*methyl*-5,5-*diphenyl*-4,5-*dihydrofuran*-3-*carboxylate* **4aa**. Liquid (Found: m/z 308.1412. Calc. for $C_{20}H_{20}O_3$: M, 308.1376); $\nu_{max}(CHCl_3)$/cm^{-1} 1685 (C=O); δ_H(90 MHz; $CDCl_3$) 1.23 (3 H, t, J 7.0, CH_2CH_3), 2.33 (3 H, t, J 1.2, Me), 3.57 (2 H, q, J 1.2, CH_2), 4.10 (2 H, q, J 7.0, OCH_2CH_3) and 7.17–7.50 (10 H, m, 2 × Ph); δ_C(22.5 MHz; $CDCl_3$) 166.00 (C=O), 165.45 (2-C), 145.02 (>C=), 128.11 (=CH–), 127.27 (=CH–), 125.45 (=CH–), 101.60 (3-C), 91.34 (5-C), 59.28 (OCH_2CH_3), 43.99 (4-C), 14.22 (Me) and 13.99 (Me); m/z 308 (M^+, 30%), 262 (100), 247 (43), 191 (85) and 43 (34).

Benzophenone **5a**. M.p. 48 °C (from ethanol).

2-Hydroxy-2,2-diphenylethyl acetate **6a**. M.p. 92.0–92.5 °C (from water–ethanol) (lit.,[13] m.p. 93–93.5 °C).

Ethyl 2-*methyl*-5-*phenylfuran*-3-*carboxylate* **7**. Liquid (Found: m/z 230.0941. Calc. for $C_{14}H_{14}O_3$: M, 230.0943); $\nu_{max}(CHCl_3)$/cm^{-1} 1709 (C=O); δ_H(60 MHz; $CDCl_3$) 1.36 (3 H, t, J 7.0, CH_2CH_3), 2.63 (3 H, s, Me), 4.31 (2 H, q, J 7.0, OCH_2CH_3), 6.67 (1 H, s, =CH–) and 7.20–7.81 (5 H, m, Ph).

Formation of Formaldehyde 2,4-*Dinitrophenylhydrazone.*—A mixture of **1a** (1 mmol), **2a** (3 mmol), and manganese(III) acetate (0.33 mmol) in acetic acid (25 cm^3) was stirred at 23 °C for 24 h. 2,4-Dinitrophenylhydrazine (1 mmol) and 2 mol dm^{-3} sulfuric acid (30 cm^3) were added to the mixture, which was stirred at room temperature for 0.5 h. Then, the reaction mixture was extracted with benzene (× 3), and the combined extracts were washed with a saturated aqueous sodium hydrogen carbonate, dried (Na_2SO_4) and evaporated. The residue was purified on a silica gel plate with chloroform as the eluent to give formaldehyde 2,4-dinitrophenylhydrazone (10%), m.p. 158 °C, identical with that of an authentic sample.

Reactions of Various Alkenes with β-Keto Esters in the Presence of Manganese(II) Acetate–Oxidant and Molecular Oxygen.—The general procedure for the reaction of alkenes with β-keto esters in the presence of manganese(II) acetate–oxidant and oxygen was as follows. Manganese(II) acetate (1 mmol) and an oxidant (0.1 mol. equiv.) was added to a stirred solution of an alkene **1** (1 mmol) and a β-keto ester **2** (3 mmol) in acetic acid (30 cm^3) in a three-necked flask equipped with a dry-air inlet tube. The mixture was stirred at 23 °C under a dry-air stream for the period of time shown in Tables 2 and 3. The solvent was removed under reduced pressure and the residue was triturated with 1 mol dm^{-3} sulfuric acid (30 cm^3) and then extracted with chloroform. The products were separated on TLC (Wakogel B10) with chloroform as the eluent. The products were further purified by recrystallization. Yields are listed in Tables 2 and 3.

Ethyl cis-*6,6-bis(4-fluorophenyl)-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate* **3ba**. M.p. 154 °C (from ethanol) (Found: C, 63.2; H, 5.3. Calc. for $C_{20}H_{20}F_2O_5$: C, 63.49; H, 5.32%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3644 (OH) and 1684 (C=O); δ_H(60 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 1.40 (3 H, s, Me), 1.73 (1 H, br s, OH), 2.77 (3 H, m, CH_2CH), 4.03 (2 H, q, *J* 7.0, OCH_2CH_3) and 6.77–7.67 (8 H, m, ArH).

Ethyl 5,5-bis(4-fluorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate **4ba**. Liquid (Found: *m/z* 344.1232. Calc. for $C_{20}H_{18}F_2O_3$: *M*, 344.1224); $\nu_{max}(CHCl_3)/cm^{-1}$ 1685 (C=O); δ_H(60 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 2.30 (3 H, t, *J* 1.2, Me), 3.50 (2 H, q, *J* 1.2, CH_2), 4.13 (2 H, q, *J* 7.0, OCH_2CH_3) and 7.17–7.43 (8 H, m, ArH); *m/z* 344 (M^+, 30%), 298 (100), 283 (29), 227 (41) and 43 (14).

Ethyl cis-*6,6-Bis(4-chlorophenyl)-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate* **3ca**. M.p. 135–137 °C (from ethanol) (Found: C, 58.5; H, 4.9. Calc. for $C_{20}H_{20}Cl_2O_5$: C, 58.41; H, 4.90%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3604 (OH) and 1730 (C=O); δ_H(90 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 1.40 (3 H, s, Me), 2.77 (3 H, m, CH_2CH), 2.87–3.53 (1 H, br s, OH), 4.17 (2 H, q, *J* 7.0, OCH_2CH_3) and 7.17–7.67 (8 H, m, ArH); δ_C(22.5 MHz; $CDCl_3$) 171.19 (C=O), 141.21 (=CCl–), 138.99 (=CCl–), 134.10 (=C<), 133.49 (=C<), 128.76 (=CH–), 128.53 (=CH–), 128.14 (=CH–), 127.23 (=CH–), 98.95 (3-C), 84.43 (6-C), 61.38 (OCH_2CH_3), 45.24 (4-C), 31.49 (5-C), 24.45 (Me) and 14.03 (CH_2CH_3).

4,4′-Dichlorobenzophenone **5c**, m.p. 146–147 °C (from benzene–hexane).

Ethyl cis-*3-hydroxy-3-methyl-6,6-bis(4-methylphenyl)-1,2-dioxane-4-carboxylate* **3da**. M.p. 152–153 °C (from ethanol) (Found: C, 71.1; H, 7.0. Calc. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.08%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 (OH) and 1729 (C=O); δ_H(90 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 1.43 (3 H, s, Me), 2.27 (3 H, s, Me), 2.33 (3 H, s, Me), 2.82 (3 H, m, CH_2CH), 3.85 (1 H, br s, OH), 4.17 (2 H, q, *J* 7.0, OCH_2CH_3) and 7.03–7.47 (8 H, m, ArH); δ_C(22.5 MHz; $CDCl_3$) 171.59 (C=O), 140.52 (=C<), 137.92 (=C<), 137.76 (=C<), 136.91 (=C<), 129.14 (=CH–), 128.97 (=CH–), 126.63 (=CH–), 125.77 (=CH–), 98.44 (3-C), 85.06 (6-C), 61.19 (–OCH_2CH_3), 45.52 (4-C), 31.80 (5-C), 24.43 (Me), 21.02 (Me), 20.97 (Me) and 14.11 (CH_2CH_3).

Ethyl 2-methyl-5,5-bis(4-methylphenyl)-4,5-dihydrofuran-3-carboxylate **4da**. Liquid (Found: *m/z* 336.1714. Calc. for $C_{22}H_{24}O_3$: *M*, 336.1726); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O); δ_H(60 MHz; $CDCl_3$) 1.20 (3 H, t, *J* 7.0, CH_2CH_3), 2.27 (6 H, s, 2 × Me), 2.33 (3 H, t, *J* 1.6, Me), 3.47 (2 H, q, *J* 1.6, CH_2), 4.07 (2 H, q, *J* 7.0, OCH_2CH_3) and 7.03–7.93 (8 H, m, ArH); *m/z* 336 (M^+, 19%), 294 (100), 219 (97) and 43 (13).

Ethyl cis-*3-hydroxy-6,6-bis(4-methoxyphenyl)-3-methyl-1,2-dioxane-4-carboxylate* **3ea**. M.p. 122–123 °C (from ethanol) (Found: C, 65.6; H, 6.55. Calc. for $C_{22}H_{26}O_7$: C, 65.66; H, 6.51%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3596 (OH) and 1727 (C=O); δ_H(60 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 1.40 (3 H, s, Me), 2.83 (3 H, m, CH_2CH), 3.80 (6 H, s, OMe), 3.95 (1 H, br s, OH), 4.23 (2 H, q, *J* 7.0, OCH_2CH_3) and 7.03–7.93 (8 H, m, ArH).

Ethyl 5,5-bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate **4ea**. Liquid (Found: *m/z* 368.1644. Calc. for $C_{22}H_{24}O_5$: *M*, 368.1624); $\nu_{max}(CHCl_3)/cm^{-1}$ 1682 (C=O); δ_H(60 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.0, CH_2CH_3), 2.33 (3 H, t, *J* 1.6, Me), 3.47 (2 H, q, *J* 1.6, CH_2), 3.87 (6 H, s, 2 × OMe), 4.10 (2 H, q, *J* 7.0, OCH_2CH_3) and 6.67–7.30 (8 H, m, ArH); *m/z* 368 (M^+, 36%), 322 (61), 307 (13), 251 (90) and 43 (9).

Ethyl cis-*3-hydroxy-3-methyl-6-phenyl-1,2-dioxane-4-carboxylate* **3fa**. M.p. 89 °C (from benzene–hexane) (Found: C, 63.2; H, 6.8. Calc. for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3488 (OH) and 1729 (C=O); δ_H(90 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 1.55 (3 H, s, Me), 2.09 (1 H, ddd, *J* 2, 5 and 15, 5-H_{eq}), 2.47 (1 H, ddd, *J* 12, 13 and 15, 5-H_{ax}), 3.10 (1 H, dd, *J* 5 and 12, 4-H), 3.60–3.90 (1 H, br s, OH), 4.23 (2 H, q, *J* 7.0, OCH_2CH_3), 5.14 (1 H, dd, *J* 2 and 13, 6-H) and 7.17–7.50 (5 H, m, Ph); δ_C(22.5 MHz; $CDCl_3$) 171.34 (C=O), 137.07 (=C<), 128.99 (=CH–), 128.61 (=CH–), 127.11 (=CH–), 98.56 (3-C), 81.77 (6-C), 61.28 (OCH_2CH_3), 48.45 (4-C), 29.29 (5-C), 24.48 (Me) and 14.11 (CH_2CH_3).

Ethyl 2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate **4fa**. Liquid (Found: *m/z* 232.1099. Calc. for $C_{14}H_{16}O_3$: *M*, 232.1099); $\nu_{max}(CHCl_3)/cm^{-1}$ 1691 (C=O); δ_H(60 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7.0, CH_2CH_3), 2.23 (3 H, t, *J* 1.6, Me), 2.83 (2 H, m, CH_2), 4.10 (2 H, q, *J* 7.0, OCH_2CH_3), 5.33–5.67 (1 H, m, *CH*Ph) and 7.20–7.70 (5 H, m, Ph).

Ethyl cis-*3-hydroxy-3-methyl-*t*-5,*c*-6-diphenyl-1,2-dioxane-4-carboxylate* **3ga**. M.p. 89 °C (from benzene–hexane) (Found: C, 69.9; H, 6.5. Calc. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3592 (OH) and 1729 (C=O); δ_H(90 MHz; $CDCl_3$) 0.98 (3 H, t, *J* 7.0, CH_2CH_3), 1.58 (3 H, s, Me), 3.27 (1 H, d, *J* 12.0, 4-H), 3.75–4.20 (1 H, br s, OH), 3.81 (1 H, dd, *J* 10.7 and 12.0, 5-H), 3.95 (2 H, q, *J* 7.0, OCH_2CH_3), 5.12 (1 H, d, *J* 10.7, 6-H) and 6.80–7.75 (10 H, m, 2 × Ph).

2-Hydroxy-1,2,2-triphenylethyl acetate **6i**. M.p. 226 °C (from benzene) (lit.,[14] m.p. 224.5–225.5 °C).

Methyl cis-*3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate* **3ab**. M.p. 183–184 °C (from ethanol) (Found: C, 69.6; H, 6.2. Calc. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3596 (OH) and 1731 (C=O); δ_H(60 MHz; $CDCl_3$) 1.40 (3 H, s, Me), 2.87 (3 H, m, CH_2CH), 3.70 (3 H, s, OMe), 3.90 (1 H, s, OH) and 7.17–7.87 (10 H, m, 2 × Ph).

Propyl cis-*3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate* **3ac**. M.p. 140–141 °C (from ethanol) (Found: C, 70.8; H, 6.8. Calc. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.73%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3596 (OH) and 1728 (C=O); δ_H(60 MHz; $CDCl_3$) 0.93 (3 H, t, *J* 7.0, CH_2CH_3), 1.40 (3 H, s, Me), 1.67 (2 H, m, $CH_2CH_2CH_3$), 2.87 (3 H, m, CH_2CH), 4.00 (1 H, s, OH), 4.10 (2 H, t, *J* 7.0, OCH_2) and 7.10–7.77 (10 H, m, 2 × Ph).

Butyl cis-*3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate* **3ad**. M.p. 121–122 °C (from ethanol) (Found: C, 71.4; H, 7.0. Calc. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.08%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3529 (OH) and 1725 (C=O); δ_H(60 MHz; $CDCl_3$) 0.70–2.00 (7 H, m, $CH_2CH_2CH_3$), 1.40 (3 H, s, Me), 2.80 (3 H, m, CH_2CH), 3.87 (1 H, s, OH), 4.13 (2 H, t, *J* 7.0, OCH_2CH_2) and 7.10–7.73 (10 H, m, 2 × Ph).

tert-*Butyl* cis-*3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate* **3ae**. M.p. 120 °C (from ethanol) (Found: C, 71.2; H, 7.05. Calc. for $C_{22}H_{26}O_5$: C, 71.33; H, 7.08%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3596 (OH) and 1721 (C=O); δ_H(60 MHz; $CDCl_3$); δ 1.37 (3 H, s, Me), 1.47 (9 H, s, CMe_3), 2.80 (3 H, m, CH_2CH), 4.13 (1 H, br s, OH) and 7.03–7.63 (10 H, m, 2 × Ph).

Ethyl cis-*3-hydroxy-3,6,6-triphenyl-1,2-dioxane-4-carboxylate*

3af. M.p. 163 °C (from ethanol) (Found: C, 74.2; H, 6.0. Calc. for $C_{25}H_{24}O_5$: C, 74.09; H, 5.95%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3610 (OH) and 1740 (C=O); δ_H(90 MHz; $CDCl_3$) 0.97 (3 H, t, *J* 7.0, CH_2CH_3), 2.90–3.17 (3 H, m, CH_2CH), 3.97 (2 H, q, *J* 7.0, OCH_2CH_3), 4.30–4.83 (1 H, br s, OH) and 7.13–7.83 (15 H, m, 3 × Ph); δ_C(22.5 MHz; $CDCl_3$) 171.11 (C=O), 142.85 (=C<), 140.71 (=C<), 138.95 (=C<), 129.09 (=CH–), 128.60 (=CH–), 128.41 (=CH–), 128.18 (=CH–), 128.05 (=CH–), 127.51 (=CH–), 126.97 (=CH–), 126.08 (=CH–), 99.42 (3-C), 85.43 (6-C), 61.07 (OCH_2CH_3), 46.42 (4-C), 32.46 (5-C) and 13.74 (CH_2CH_3).

6-Hydroxy-6-methyl-9,9-diphenyl-2,7,8-trioxaspiro[4.5]decan-1-one **3ag**. M.p. 207–209 °C (from ethanol) (Found: C, 70.6; H, 5.9. Calc. for $C_{20}H_{20}O_5$: C, 70.27; H, 5.92%); ν_{max}(KBr)/cm^{-1} 3464 (OH) and 1733 (C=O); δ_H[90 MHz; $(CD_3)_2SO$] 1.60 (3 H, s, Me), 2.80–3.17 (2 H, m, CH_2), 3.30 (1 H, s, OH), 3.77–4.23 [4 H, m, $(CH_2)_2$] and 6.83–7.77 (10 H, m, 2 × Ph); δ_C[22.5 MHz; $(CD_3)_2SO$] 177.61 (C=O), 143.61 (=C<), 142.36 (=C<), 128.07 (=CH–), 127.81 (=CH–), 127.53 (=CH–), 126.71 (=CH–), 126.20 (=CH–), 125.32 (=CH–), 101.38 (6-C), 83.70 (9-C), 67.16 (3-C), 48.65 (C-5), 39.82 (>CH_2), 30.57 (>CH_2) and 21.33 (Me).

Ethyl 1-hydroxy-4,4-diphenyl-2,3-dioxabicyclo[4.3.0]nonane-6-carboxylate **3ah**. M.p. 128 °C (from ethanol) (Found: C, 71.7; H, 6.6. Calc. for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3360 (OH) and 1706 (C=O); δ_H(90 MHz; $CDCl_3$) 1.13 (3 H, t, *J* 7.0, CH_2CH_3), 1.27–2.27 [6 H, m, $(CH_2)_3$], 2.71 (1 H, d, *J* 14, 5-H), 3.24 (1 H, d, *J* 14, 5-H), 3.73 (2 H, q, *J* 7.0, OCH_2CH_3), 6.80 (1 H, s, OH) and 7.10–7.63 (10 H, m, 2 × Ph); δ_C(22.5 MHz; $CDCl_3$) 175.87 (C=O), 145.65 (=C<), 142.82 (=C<), 128.32 (=CH–), 128.06 (=CH–), 127.17 (=CH–), 127.11 (=CH–), 125.47 (=CH–), 125.41 (=CH–), 111.16 (1-C), 83.95 (4-C), 61.09 (OCH_2CH_3), 50.40 (6-C), 39.96 (>CH_2), 35.96 (>CH_2), 35.41 (>CH_2), 20.14 (>CH_2) and 13.59 (CH_2CH_3).

Ethyl 1-acetoxy-3,3-diphenyl-2-oxabicyclo[3.3.0]octane-5-carboxylate **8**. Liquid (Found: *m/z* 394.1823. Calc. for $C_{24}H_{26}O_5$: *M*, 394.1780); $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (C=O); δ_H(60 MHz; $CDCl_3$) 1.13 (3 H, t, *J* 7.0, CH_2CH_3), 1.40 (3 H, s, OAc), 1.67–2.37 [6 H, m, $(CH_2)_3$], 2.58 (1 H, d, *J* 12, 4-H), 3.75 (1 H, d, *J* 12, 4-H), 4.07 (2 H, q, *J* 7.0, OCH_2CH_3) and 6.90–7.53 (10 H, m, 2 × Ph); δ_C(22.5 MHz; $CDCl_3$) 172.26 (C=O), 168.97 (C=O), 147.29 (=C<), 147.10 (=C<), 128.35 (=CH–), 128.08 (=CH–), 126.48 (=CH–), 126.38 (=CH–), 125.38 (=CH–), 124.48 (=CH–), 118.77 (1-C), 90.58 (3-C), 64.14 (5-C), 60.14 (OCH_2CH_3), 45.84 (>CH_2), 35.59 (>CH_2), 34.89 (>CH_2), 22.81 (>CH_2), 21.06 ($COCH_3$) and 14.02 (CH_2CH_3); *m/z* 394 (M^+, 38%), 335 (36), 334 (100), 288 (35) and 257 (60).

Diethyl 2,2'-dioxobicyclopentyl-1,1'-dicarboxylate **9**. M.p. 53–54 °C (from hexane) (Found: C, 62.1; H, 7.25. Calc. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (C=O); δ_H(60 MHz; $CDCl_3$) 1.37 (6 H, t, *J* 7.0, 2 × CH_2CH_3), 1.63–3.13 [12 H, m, 2 × $(CH_2)_3$] and 4.33 (4 H, q, *J* 7.0, 2 × OCH_2CH_3).

Ethyl 1-hydroxy-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decane-6-carboxylate **3ai**. M.p. 128 °C (from ethanol) (Found: C, 72.1; H, 6.85. Calc. for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3364 (OH) and 1719 (C=O); δ_H(60 MHz; $CDCl_3$) 1.03 (3 H, t, *J* 7.0, CH_2CH_3), 1.33–2.33 [8 H, m, $(CH_2)_4$], 2.70 (1 H, d, *J* 12, 5-H), 3.20 (1 H, d, *J* 12, 5-H), 3.80 (2 H, q, *J* 7.0, OCH_2CH_3), 6.73 (1 H, s, OH) and 6.97–7.66 (10 H, m, 2 × Ph).

Diethyl 2,2'-dioxobicyclohexyl-1,1'-dicarboxylate **10**. M.p. 106–107 °C (from benzene–hexane) (Found: *m/z* 338.1736. Calc. for $C_{18}H_{26}O_6$: *M*, 338.1729); $\nu_{max}(CHCl_3)/cm^{-1}$ 1729 (C=O); δ_H(60 MHz; $CDCl_3$) 1.33 (6 H, t, *J* 7.0, 2 × CH_2CH_3), 1.50–3.00 [16 H, m, 2 × $(CH_2)_4$] and 4.27 (4 H, q, *J* 7.0, 2 × OCH_2CH_3); *m/z* 338 (M^+, 9%), 292 (18), 247 (32), 219 (32), 191 (25), 170 (100) and 124 (39).

Methylation of Ethyl cis-*3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate* **3aa**.—Camphor-10-sulfonic acid (668 mg) was added to a solution of **3aa** (186 mg) dissolved in methanol (5 cm^3) and the mixture was heated at 50 °C for 27 h. Saturated aqueous sodium hydrogen carbonate (10 cm^3) was added to the reaction mixture which was then extracted with chloroform (30 cm^3). The extract was separated, dried (Na_2SO_4) and evaporated. The residue was purified by TLC (Wakogel B10) with chloroform as the eluent to give a mixture of ethyl *t*-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane-*r*-4-carboxylate **11aa** and ethyl *c*-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane-*r*-4-carboxylate **11aa'** (179 mg, 92%) (molar ratio; 3:1).

Ethyl 3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylates **11aa** *and* **11aa'**. M.p. 118–119 °C (from hexane) (Found: C, 70.5; H, 6.8. Calc. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1729 (C=O); δ_H(60 MHz; $CDCl_3$) 1.27 (3 H, t, *J* 7.0, CH_2CH_3), 1.30 and 1.37 (3 H, s, s, Me), 2.63–3.10 (3 H, m, CH_2CH), 3.43 and 3.88 (3 H, s, s, OMe), 4.20 (2 H, q, *J* 7.0, OCH_2CH_3) and 7.23–7.73 (10 H, m, 2 × Ph); δ_C(22.5 MHz; $CDCl_3$) 170.61 (C=O), 143.67 (=C<), 141.15 (=C<), 128.41 (=CH–), 128.29 (=CH–), 128.20 (=CH–), 127.93 (=CH–), 127.68 (=CH–), 127.29 (=CH–), 127.05 (=CH–), 126.32 (=CH–), 126.24 (=CH–), 125.93 (=CH–), 101.32 (3-C), 85.50 (6-C), 60.83 (OCH_2CH_3), 50.00 and 49.21 (OMe), 46.255 (4-C), 34.37 and 31.15 (5-C), 19.42 (CH_2CH_3), 15.53 and 14.14 (Me).

Reactions of **11aa** *and* **11aa'** *with Grignard Reagents*.—An ethereal solution of **11aa** and **11aa'** was added dropwise to a stirred solution of a Grignard reagent (MeMgI or PhMgBr) in dry diethyl ether (3 cm^3) at 35 °C under an atmosphere of argon for 30 min. The mixture was stirred under reflux for 2 h. The reaction mixture was treated with aqueous ammonium chloride and ether. The ether layer was separated and the aqueous layer was extracted with ether several times. The combined ether extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was purified by TLC (Wakogel B10) eluting with a mixture of ether–hexane (1:9, v/v).

4-(1-Hydroxy-1-methylethyl)-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane **12**. Liquid (34%) (Found: *m/z* 342.1830. Calc. for $C_{21}H_{26}O_4$: *M*, 342.1831); $\nu_{max}(CHCl_3)/cm^{-1}$ 3516 (OH); δ_H(90 MHz; $CDCl_3$) 1.29 (3 H, s, Me), 1.34 (3 H, s, Me), 1.37 (3 H, s, Me), 1.95 (1 H, H_A) and 2.69 (2 H, H_B) (CH_2CH, AB_2 spin system, J_{AB} 7.8), 3.05 (1 H, s, OH), 3.45 (3 H, s, OMe) and 7.10–7.62 (10 H, m, 2 × Ph); δ_C(22.5 MHz; $CDCl_3$) 144.59 (=C<), 142.09 (=C<), 128.35 (=CH–), 128.19 (=CH–), 127.65 (=CH–), 127.07 (=CH–), 127.01 (=CH–), 126.01 (=CH–), 104.44 (3-C), 85.85 (6-C), 71.52 (CMe_2OH), 48.89 (–OMe), 48.41 (4-C), 31.97 (Me), 31.45 (5-C), 28.52 (Me) and 22.42 (Me).

4-(Hydroxydiphenylmethyl)-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane **13**. Colourless needles (33%; from methanol), m.p. 171–172 °C [Found: *m/z* 489.2041 (M^+ + Na). Calc. for $C_{31}H_{30}NaO_4$: *M*, 489.2042]; $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 (OH); δ_H(90 MHz; $CDCl_3$) 0.57 (3 H, s, Me), 2.33–3.05 (3 H, m, CH_2CH), 3.45 (3 H, s, OMe), 5.25 (1 H, s, OH) and 6.9–7.7 (20 H, m, 4 × Ph); δ_C(22.5 MHz; $CDCl_3$) 151.438, 147.918, 146.217, 143.711, 141.742, 128.361, 128.301, 128.077, 128.003, 127.854, 127.466, 127.242, 127.108, 126.541, 126.466, 126.332, 125.720, 125.094, 105.119 (3-C), 86.935 (6-C), 78.208 (O–C), 48.910 (OMe), 46.449 (4-C), 30.830 (5-C) and 21.000 (Me); *m/z* 489 (M^+ + Na, 10%), 329 (10), 299 (15), 251 (10), 183 (65) and 105 (100).

Decomposition of **3aa** *with Perchloric Acid in Acetic Acid*.—A mixture of **3aa** (0.1 mmol) and 60% perchloric acid (0.01 cm^3) in acetic acid (10 cm^3) was stirred at room temperature for 1 h. After dilution with water (10 cm^3) the mixture was extracted with diethyl ether and the extract evaporated. The residue was purified on a silica gel plate eluting with chloroform to give **7** in quantitative yield.

MM2 Calculations.—These were performed by Chem 3D Plus (Version 3.0) using standard measurements. By considering an anomeric effect for the 1,2-dioxan-3-ol ring, the conformations, which might have the lowest energy, were calculated. The results were shown in Fig. 3.

Acknowledgements

We thank the Referees for their suggestions, particularly on the reaction mechanisms, and also thank Mr. Yasunori Sudo and the staff of the Taiho Pharmaceutical Co. Inc., Tokushima, Japan, for the measurements of high-resolution mass spectra.

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Paper 2/04764K
Received 4*th September* 1992
Accepted 27*th November* 1992