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Manganese(II and III)-Mediated Synthesis of Cyclic Peroxides from Alkenes, Active Methylene Compounds, and Molecular Oxygen

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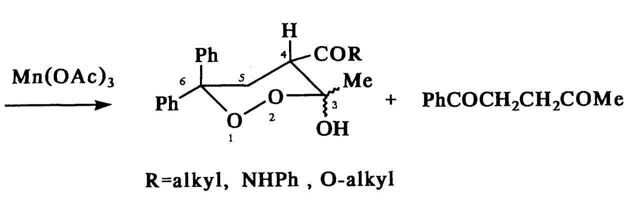
The reaction of 1,1-diphenylethene, 1,1-bis(4-chlorophenyl)ethene, 1,1-bis(4-methylphenyl)ethene, 1,1-bis(4-methoxyphenyl)ethene, and 1,1-bis(4-fluorophenyl)ethene with 2-methyl-1,3-cyclohexanedione, 2-methyl-1,3-cyclopentanedione, 2-acetylcyclohexanone, ethyl 2-acetyl-3-oxobutanoate, 3-methyl-2,4-pentanedione, 1,3-cyclohexanedione, and 2,4-pentanedione in the presence of $Mn(OAc)_2$ and molecular oxygen yielded the corresponding cyclic peroxides in moderate-to-good yields. Similar reaction of 1,1-disubstituted alkenes with 1,3-cyclopentanedione in the presence of $Mn(OAc)_3$ and molecular oxygen gave 2,2,9,9-tetraphenyloctahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diols. Acid-catalyzed decomposition of 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols yielded 3-acetyl-5-aryl-2-methylfurans in moderate yields. Treatment of the 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols with alkali gave 6,6-diaryl-3-methyl-1,2-dioxan-3-ols which gave 1-aryl-1,4-pentanediones upon treatment with hydrochloric acid in acetic acid. The synthetic utility and mechanisms of the reactions are discussed.

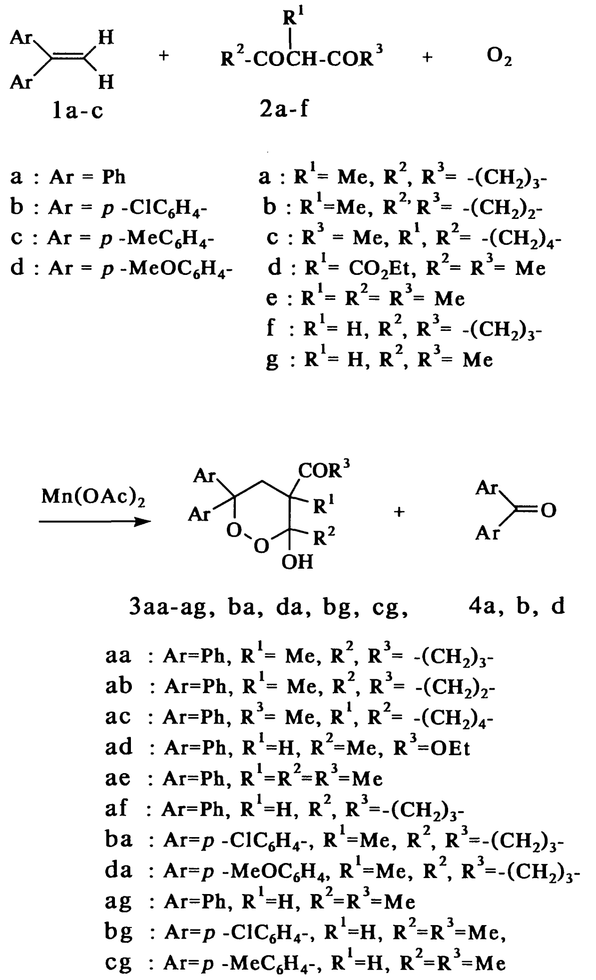
For some years there has been growing interest in 1,2-dioxane derivatives as synthetic and biologically active compounds.[1] In previous papers[2] we reported the facile syntheses of substituted 1,2-dioxan-3-ols by $Mn(OAc)_3$-mediated reaction of alkenes with 1,3-dicarbonyl compounds, such as 1,3-diketones, acetoacetamides and *β*-keto esters, and molecular oxygen (O_2) (Scheme 1). In the reaction of alkenes with acetoacetamide, it was found that $Mn(OAc)_2$ was as effective as $Mn(OAc)_3$.[2c] We investigated the $Mn(OAc)_2$-mediated reaction of 1,1-diarylethenes (**1a**—**e**) with various 1,3-diketones in the presence of O_2 that gave various cyclic peroxides; further, the $Mn(OAc)_3$-catalyzed reaction of alkenes with 1,3-cyclopentanedione yielded 2,2,9,9-tetraaryloctahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diols. We found that the acid-catalyzed decomposition of 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols and 6,6-diaryl-3-methyl-1,2-dioxan-3-ols yielded substituted furans and 1-aryl-1,4-pentanediones, respectively, both involving aryl migration. This could be accounted for in terms of an acid-catalyzed oxygen-oxygen bond cleavage, followed by aryl migration and, in case of furan formation, recyclization. We scrutinized the reactions and describe the results in this paper.



Scheme 1.

Results and Discussion

Reactions of 1,1-Disubstituted Ethenes (1a—d) in the Presence of Metal Acetate-O_2. The reactions were examined with several metal acetates, such as $Mn(OAc)_2$, $Mn(OAc)_3$, $Co(OAc)_2$, and $Co(OAc)_3$. When a mixture of 1,1-diphenylethene (**1a**), 2-methyl-1,3-cyclohexanedione (**2a**), and a metal acetate was stirred in acetic acid under a current of dried air at 23 °C, the product was found to comprise 1-hydroxy-6-methyl-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-7-one (**3aa**) and benzophenone (**4a**). The sturctures of **3aa** and **4a** were elucidated by the ^1H, ^{13}C NMR and IR spectra, as well as an elemental analysis; further, their spectra were compared with an authentic specimen (Scheme 2). The maximum yield for **3aa** was attained from the reaction of $Mn(OAc)_2$ at a molar ratio of 1 : 3 : 1 (Table 1, Entry 1). It was also observed that the reaction at a molar ratio of 1 : 3 : 0.5 yielded **3aa** and **4a** in comparable yields (Entry 2). The reactions were then examined for **1a**, 1,1-bis(4-chlorophenyl)ethene (**1b**), 1,1-bis(4-methylphenyl)ethene (**1c**), and 1,1-bis(4-methoxyphenyl)ethene (**1d**) with **2a** and various 1,3-diketones, such as 2-methyl-1,3-cyclopentanedione (**2b**), 2-acetylcyclohexanone (**2c**), ethyl 2-acetyl-3-oxobutanoate (**2d**), 3-methyl-2,4-pentanedione (**2e**), 1,3-cyclohexanedione (**2f**), and 2,4-pentanedione (**2g**). The reactions gave the corresponding cyclic peroxides (**3ab**—**3cg**), which are shown in Scheme 2 and Table 1. The reaction of **1a** and **2d** yielded 4-ethoxycarbonyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3ad**) with the loss of an acetyl group. The yields for 1,2-dioxan-3-ols (**3ag**—**cg**) from reactions of 2,4-pentanedione (**2g**) with 1,1-disubstituted ethenes (**1a**—**c**) in the presence of $Mn(OAc)_2$ were lower than those of $Mn(OAc)_3$ which has been shown to be an excellent catalyst for the formal [2+2+2] cycloaddition of molecular oxygen, alkene, and 1,3-dicarbonyl compounds.[2)]



a : Ar = Ph
b : Ar = p-ClC_6H_4-
c : Ar = p-MeC_6H_4-
d : Ar = p-$MeOC_6H_4$-

a : R^1= Me, R^2, R^3= -$(CH_2)_3$-
b : R^1=Me, R^2, R^3= -$(CH_2)_2$-
c : R^3 = Me, R^1, R^2= -$(CH_2)_4$-
d : R^1= CO_2Et, R^2= R^3= Me
e : R^1= R^2= R^3= Me
f : R^1= H, R^2, R^3= -$(CH_2)_3$-
g : R^1= H, R^2, R^3= Me

aa : Ar=Ph, R^1= Me, R^2, R^3= -$(CH_2)_3$-
ab : Ar=Ph, R^1= Me, R^2, R^3= -$(CH_2)_2$-
ac : Ar=Ph, R^3= Me, R^1, R^2= -$(CH_2)_4$-
ad : Ar=Ph, R^1=H, R^2=Me, R^3=OEt
ae : Ar=Ph, R^1=R^2=R^3=Me
af : Ar=Ph, R^1=H, R^2, R^3=-$(CH_2)_3$-
ba : Ar=p-ClC_6H_4-, R^1=Me, R^2, R^3=-$(CH_2)_3$-
da : Ar=p-$MeOC_6H_4$, R^1=Me, R^2, R^3=-$(CH_2)_3$-
ag : Ar=Ph, R^1=H, R^2=R^3=Me
bg : Ar=p-ClC_6H_4-, R^1=H, R^2=R^3=Me,
cg : Ar=p-MeC_6H_4-, R^1=H, R^2=R^3=Me

Scheme 2.

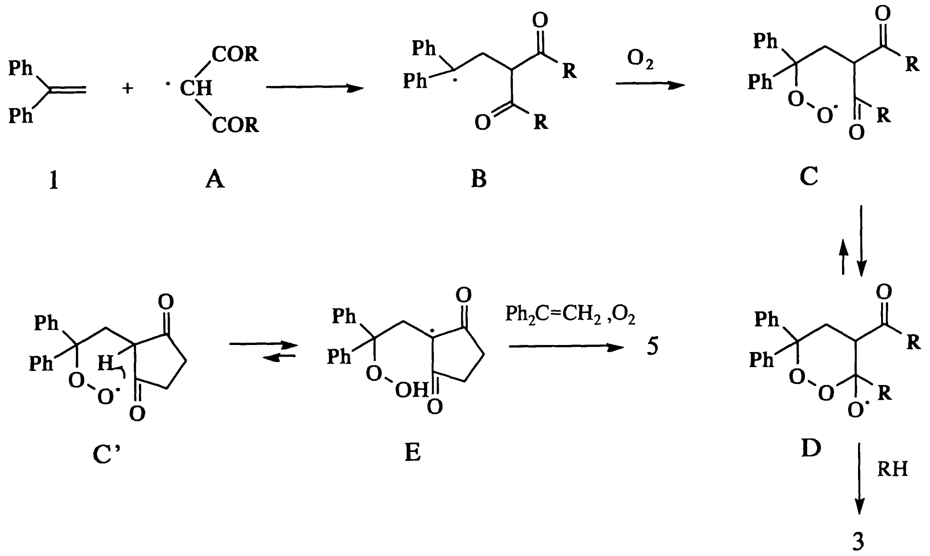
The present Mn(OAc)$_2$-mediated reaction could be accounted for by a mechanism similar to that for the Mn(OAc)$_3$-mediated reaction of alkenes with 1,3-diketones.[2a,2b)] Aerial oxidation of Mn(II) could produce a catalytic amount of Mn(III),[3)] which reacts with 1,3-diketones to give dicarbonylmethyl radicals (**A**). Then, **A** attacks alkenes to form stable carbon radicals (**B**) (Scheme 3). It seemed that **B** reacted selectively with oxygen to give peroxyl radicals (**C**), rather than being oxidized to the corresponding carbocations when the concentration of Mn(III) was low; **C** cyclized to **D** and eventually yielded **3**. The carbocation can be formed in Mn(OAc)$_3$-mediated oxidation[2b)] and cyclized to give dihydrofuran derivatives, which are always found as a minor product in a reaction using Mn(III). However, the present reaction did not give any dihydrofuran derivatives. It should be interesting to note that the reaction of **1a** and **2c** gave 6-acetyl-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-1-ol (**3ac**), in which cyclization took place at the carbonyl group in the cyclohexanone ring. This could possibly be due to an energetically more favorable structure of **3ac** than a spiroundecanone (**3ac′**) (Fig. 1). In order to confirm our view, MM2 calculations were carried out in order to determine the relative stabilities of the several possible conformations of **3ac** and **3ac′**. The results showed that **3ac** should have a lower energy than **3ac′**, as is shown in Fig. 1. The stereochemistry of **3ac** could not be determined by either spectroscopy or MM2 calculations, in which *cis*- and *trans*-**3ac** had a similar relative stability. The reaction of **1a** and **2d** yielded 4-ethoxycarbonyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3ad**) (Entry 8), in which one of the acetyl groups in **2d** was lost. The reason is not presently clear.

The reactions of **1a** with active methine compounds,

Table 1. Reactions of 1,1-Disubstituted Ethenes (**1a**—**d**) with 1,3-Diketones (**2a**—**g**) and Molecular Oxygen in the Presence of metal Acetate[a)]

Entry	Alkene	Oxidant	1,3-Diketone	Molar ratio[b)]	Time / h	Composition of product (yield/%)[c)]		
1	**1a**	Mn(OAc)$_2$	**2a**	1:3:1	13		**3aa** (75)	**4a** (10)
2	**1a**	Mn(OAc)$_2$	**2a**	1:3:0.5	12		**3aa** (68)	**4a** (21)
3	**1a**	Mn(OAc)$_3$	**2a**	1:3:1	13		**3aa** (64)	**4a** (22)
4	**1a**	Co (OAc)$_2$	**2a**	1:3:1	12		**3aa** (67)	**4a** (15)
5	**1a**	Co (OAc)$_3$	**2a**	1:3:1	13		**3aa** (61)	**4a** (19)
6	**1a**	Mn(OAc)$_2$	**2b**	1:3:1	15		**3ab** (93)	**4a** (5)
7	**1a**	Mn(OAc)$_2$	**2c**	1:3:1	11		**3ac** (67)	**4a** (15)
8	**1a**	Mn(OAc)$_2$	**2d**	1:3:1	12		**3ad** (48)	**4a** (28)
9	**1a**	Mn(OAc)$_2$	**2e**	1:3:1	12		**3ae** (66)	**4a** (8)
10	**1a**	Mn(OAc)$_2$	**2f**	1:3:1	13		**3af** (79)	**4a** (11)
11	**1b**	Mn(OAc)$_2$	**2a**	1:3:1	12		**3ba** (60)	**4b** (11)
12	**1d**	Mn(OAc)$_2$	**2a**	1:3:1	12		**3da** (54)	**4d** (9)
13	**1a**	Mn(OAc)$_2$	**2g**	1:3:1	39	**1a** (85)	**3ag** (7)	
14	**1b**	Mn(OAc)$_2$	**2g**	1:3:1	12	**1b** (84)	**3bg** (6)	
15	**1c**	Mn(OAc)$_2$	**2g**	1:3:1	12	**1c** (78)	**3cg** (11)	

a) The reactions were carried out in acetic acid under a dry-air stream at 23 °C. b) **1**:**2**:metal acetate. c) Yields based on the amount of **1** used.



Scheme 3.

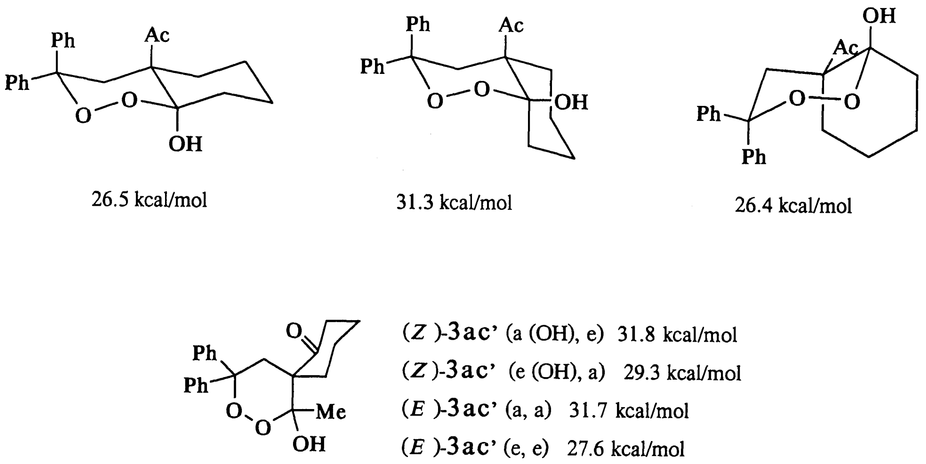
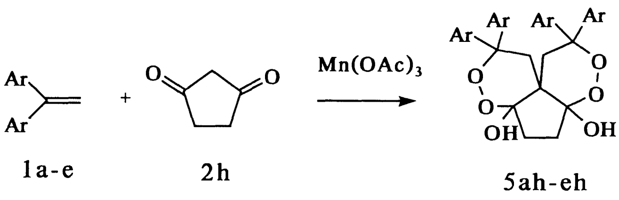


Fig. 1.

which produce tertiary carbon radicals, gave cyclic peroxides (**3aa**—**ae**) in moderate-to-good yields, while the reaction of active methylene compounds afforded poor yields of the product, except for 1,3-cyclohexanedione (**2f**) (Entry 10). Compound **1a** and 2,4-pentanedione (**2g**) gave **3ag** in a 7% yield (Entry 13). The yield was not improved by changing the alkene to **1b** and **1c** (Entries 14, 15). 1-Phenyl-1,3-butanedione and 5,5-dimethyl-1,3-cyclohexanedione gave an intractable mixture which could not be separated. This presented quite a contrast to the reactions of $Mn(OAc)_3$ with alkenes and active methylene compounds;[2)] i.e., the reactions of **1a** with **2g** and 1-phenyl-1,3-butanedione with $Mn(OAc)_3$–O_2 yielded the corresponding 1,2-dioxan-3-ols in a 81 and 43% yields, respectively.[2b)] The reactions of other alkenes, such as styrene and 2-ethyl-1-butene, with **2a** in the presence of Mn(II)–O_2 were examined, but styrene was recovered unchanged and 2-ethyl-1-butene gave no product.

Reaction of 1,1-Disubstituted Ethenes (1a—e) with 1,3-Cyclopentanedione (2h) in the Presence of $Mn(OAc)_3$-O_2. It was found that $Mn(OAc)_2$ was not effective in the reaction of 1,1-disubstituted ethenes and 1,3-cyclopentanedione (**2h**). However, the reaction of **1a** with **2h** using $Mn(OAc)_3$ yielded a product ($C_{33}H_{30}O_6$, elemental analysis). The ^{1}H NMR spectrum of this compound exhibited the presence of two methylenes at δ=1.81 and 2.63, hydroxyl groups at δ=2.81, and phenyl groups at δ=7.07—7.58. The IR spectrum also showed the presence of hydroxyl groups at ν=3568—3404. The most characteristic feature was the absence of any carbonyl signals in the ^{13}C NMR spectrum. The spectrum indicated the presence of two nonequivalent phenyl groups {δ=145.610 (>C=), 144.968 (>C=), 128.514 (-CH=), 128.320 (-CH=), 127.291 (-CH=), 126.814 (-CH=), 125.382 (-CH=), and 124.889 (-CH=)}, a carbon at δ=108.863 (>C<), a quaternary carbon at δ=48.020, and two methylene groups at δ=40.591 and

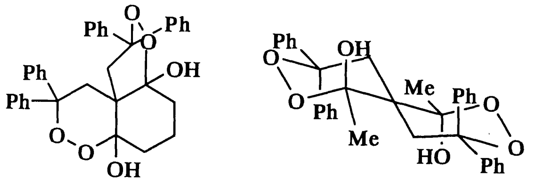
32.550. The assignments were based on its DEPT-135 spectrum. These spectroscopic data are consistent with the structure of a cyclic diperoxide: that is, 2,2,9,9-tetraphenyloctahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diol (**5ah**) (Scheme 4). The reactions were carried out at different molar ratios; it was found that the reaction at a molar ratio of 1 : 3 : 1 for **1a** : **2h**: $Mn(OAc)_3$ gave the maximum yield for **5ah**. The reactions of **1b**—**e** were examined under the same reaction conditions; the results are summarized in Table 2.



a, ah : Ar = Ph
b, bh : Ar = p-ClC_6H_4-
c, ch : Ar = p-MeC_6H_4-
d, dh : Ar = p-$MeOC_6H_4$-
e, eh : Ar = p-FC_6H_4-

Scheme 4.

The formation of cyclic diperoxide from the reactions of 1,1-disubstituted ethenes (**1a**—**e**) with 1,3-cyclopentanedione (**2h**) showed a unique feature of $Mn(OAc)_3$-mediated peroxide synthesis. In an attempt to obtain a cyclic diperoxide containing a cyclohexane ring (**I**) or a spirodiperoxide (**II**) (Fig. 2), although compounds **3af** and **3ag** were treated again with a mixture of **1a** and $Mn(OAc)_3$, no formation of the corresponding cyclic diperoxides was observed. The unreacted starting materials were recovered in both cases. It seemed that peroxyl radicals (**C′**) derived from **1a** and 1,3-cyclopentanedione (**2h**) would not cyclize to give alkoxyl radicals (**D**, R,R=-$(CH_2)_2$-) (Scheme 3), but tended to abstract the hydrogen at the α-position to the carbonly intramolecularly and to form radicals (**E**), which react with **1** and O_2 to give **5**. An attempt to obtain a monoperoxide from **1a** and **2h** was unsuccessful. The peroxyl radicals (**C**) from **1** and 1,3-cyclohexanedione (**2f**) and 2,4-pentanedione (**2g**) are in equilibrium with alkoxyl radicals (**D**), which are more stable than that from **2h**, since a bicyclo[4.4.0] ring system and a monocylic peroxide usually have a lower relative energy than a bicyclo[4.3.0] ring system, as reported by Yoshida et al.[1b]



I II

Fig. 2.

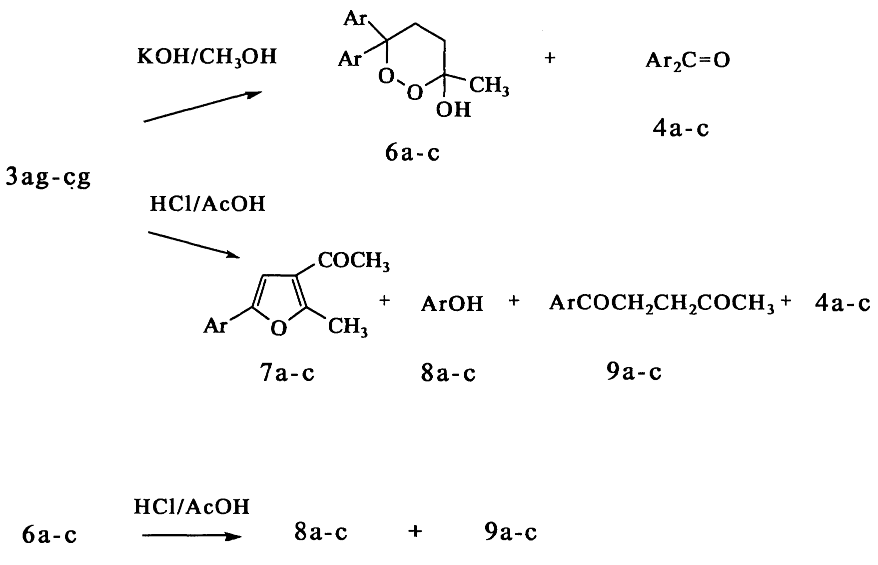
Reactions of 3ag—cg. The decomposition of cyclic peroxides have been reported using several reagents.[1b] The treatment of a cyclic peroxide with 10-camphorsulfonic acid caused a cleavage of the oxygen–oxygen bond to give a 1,4-dicarbonyl compound. A reaction with $FeSO_4$ also gave the same compound. A reaction with thiourea yielded the corresponding tetrahydrofuran derivatives. We also reported that cyclic peroxides gave dihydrofuran derivatives upon treatment with triphenylphosphine,[2b] as well as upon hydrogenation in the presence of palladium on charcoal.[2c] In contrast to the results from a base-catalyzed reaction of 1,2-dioxan-3-ols from acetoacetamides, which gave benzophenone,[2c] treatment of **3ag**–**cg** with potassium hydroxide in methanol gave 3-methyl-6,6-diphenyl-1,2-dioxan-3-ols, **6a** (Ar=phenyl), **6b** (Ar=4-chlorophenyl) and **6c** (Ar=4-methylphenyl) (Scheme 5, Table 3). It seemed that the retro-Claisen condensation by hydroxide ion, followed by recyclization, would yield **6a**—**c** (Scheme 6).

We have also been interested in the formation of 1-phenyl-1,4-pentanediones in the reaction of $Mn(OAc)_3$-mediated reaction of alkenes and **2g**, which was described in a previous report[2b] (Scheme 1). Since we believed

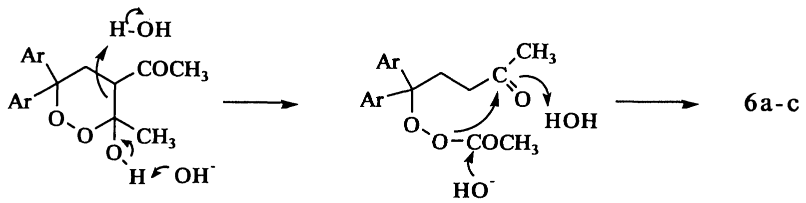
Table 2. Reaction of 1,1-Disubstituted Ethenes (**1a**—**e**)) with 1,3-Cyclopentanedione (**2h**) and Molecular Oxygen in the Presence of $Mn(OAc)_3$[a)]

Entry	Alkene	Molar ratio[b)]	Time/h	Composition of product (yield/%)[c)]	
1	**1a**	1:3:1	12		**5ah** (83)
2	**1a**	2:1:1	16	**1a** (27)	**5ah** (60)[d)]
3	**1a**	2:3:1	14	**1a** (15)	**5ah** (72)
4	**1b**	1:3:1	9		**5bh** (85)
5	**1c**	1:3:1	10		**5ch** (93)
6	**1d**	1:3:1	13		**5dh** (76)
7	**1e**	1:3:1	11		**5eh** (88)

a) The reactions were carried out in acetic acid under a dry-air stream at 23 °C. b) **1**:**2h**:$Mn(OAc)_3$. c) Yields based on the amount of **1** used. d) Yield based on the amount of **2h** used.



Scheme 5.



Scheme 6.

Table 3. Reaction of 4-Acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols (**3ag**—**cg**) with 5% KOH/MeOH[a)]

Entry	Substrate	Time h	Composition of product (yield/%)[b)]	
1	**3ag**	30	**4a** (18)	**6a** (82)
2	**3bg**	12	**4b** (30)	**6b** (68)
3	**3cg**	18	**4c** (21)	**6c** (72)

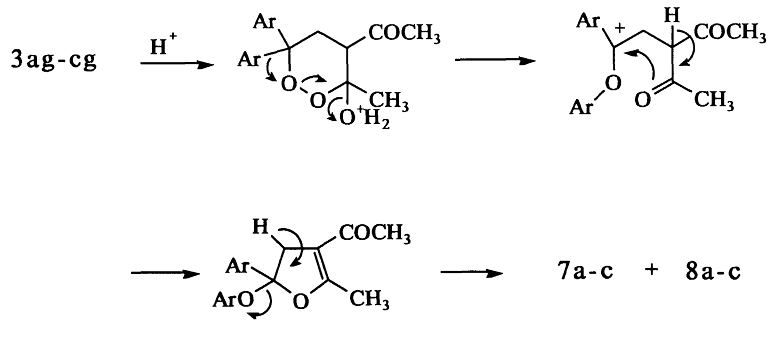
a) The reactions were carried out at the reflux temperature.
b) Yields based on the amount of **3** used.

that the 1,2-dioxan-3-ols might be decomposed during the work-up procedure using acidic conditions, **3ag** was heated in 2 M (1 M=1 mol dm^{-3}) hydrochloric acid in acetic acid. The products were separated on a silica-gel plate to give benzophenone (**4a**), 3-acetyl-2-methyl-5-phenylfuran (**7a**), phenol (**8a**), and 1-phenyl-1,4-pentanedione (**9a**). Similarly, reactions of **3bg** and **3cg** yielded the corresponding products (Scheme 5 and Table 4, Entries 1—3, where **b**: Ar=4-chlorophenyl and **c**: Ar=4-methylphenyl). Although the formation of **7a** was not expected, it could be accounted for by an acid-catalyzed oxygen-oxygen bond cleavage in **3** involving aryl migration and recyclization, followed by an elimination of phenol (Scheme 7). An acid-catalyzed decomposition of **6a**—**c** was also investigated. Compounds **9a**—**c** and phenols (**8a**—**c**) were obtained in good yields (Scheme 5, Table 4, Entries 4—6). The

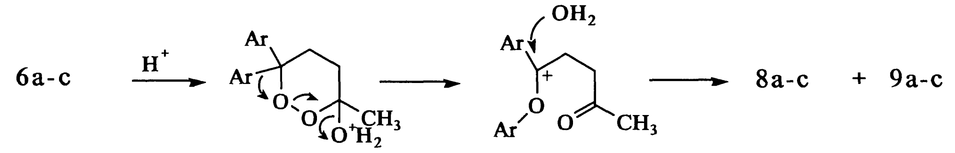
Table 4. Reactions of 4-Acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols (**3ag**—**cg**) and 6,6-Diaryl-3-methyl-1,2-dioxan-3-ols (**6a**—**c**) with 2 M HCl/AcOH

Entry	Substrate	Temp °C	Time min	Composition of product (yield/%)[a)]			
1	**3ag**	100	10	**4a** (6)	**7a** (76)	**8a** (62)	**9a** (4)
2	**3bg**	100	10	**4b** (4)	**7b** (82)	**8b** (58)	**9b** (3)
3	**3cg**	100	15	**4c** (11)	**7c** (74)	**8c** (54)	**9c** (6)
4	**6a**	80	20			**8a** (58)	**9a** (92)
5	**6b**	80	20			**8b** (63)	**9b** (84)
6	**6c**	80	20			**8c** (95)	**9c** (67)

a) Yields based on the amount of **3** or **6** used.



Scheme 7.



Scheme 8.

formation of **9a**—**c** and **8a**—**c** from **6a**—**c** could be explained in terms of mechamisms similar to those for the acid-catalyzed decomposition of **3ag**—**cg** (Scheme 8). Although compound **7a** was previously obtained by a reaction of sulfonium phenacylide with active methylene compounds,[4] our reaction would be useful for a quick two-step synthesis of 3-acetyl-5-aryl-2-methylfurans from alkenes and active methylene compounds.

Conclusion. Cyclic peroxides (**3aa**—**cg**) containing 1,2-dioxan-3-ol moiety were prepared from the $Mn(OAc)_2$-mediated reaction of alkenes, active methine compounds and molecular oxygen in better yields than the reaction with $Mn(OAc)_3$. Cyclic diperoxides **5ah**—**eh** were obtained from the reaction of 1,1-disubstituted ethenes with 1,3-cyclopentanediones (**2h**) and molecular oxygen in the presence of $Mn(OAc)_3$. A base-catalyzed decomposition of 1,2-dioxan-3-ols (**3ag**—**cg**) yielded deacetylated 1,2-dioxan-3-ols (**6a**—**c**) in good yields. An acid-catalyzed decomposition of **3ag**—**cg** and **6a**—**c** should lead to novel synthetic methods to prepare substituted furans (**7a**—**c**) and 1-aryl-1,4-pentanediones (**9a**—**c**), respectively.

Experimental

Measurements. All of the ^1H and ^{13}C spectra were taken with a JNM PMX-60SI (60 MHz) or a JNM EX-90 FT NMR (22.4 MHz for ^{13}C) spectrometer, respectively, with tetramethylsilane being used as the internal standard. The chemical shifts are shown in δ values (ppm). The IR spectra were measured on a JASCO A-102 IR spectrometer. The IR spectral data are expressed in ν values (cm^{-1}). All of the melting-moints were determined with a Yanaco micromelting-point apparatus MP-J3.

Materials. Manganese(II) acetate tetrahydrate was purchased from Wako Pure Chemical Ind. Ltd. Manganese(III) acetate dihydrate[5] was prepared according to a method described in the literature. 1,1-Diphenylethenes (**1a**—**e**) were prepared by dehydration of the corresponding alcohols, which were synthesized from substituted acetophenones and arylmagnesium bromides.[6] 1,3-Cyclopentanedione (**2h**) was prepared from 2-acetyl-1,3-cyclopentanedione.[7] Ethyl 2-acetyl-3-oxobutanoate (**2d**) was prepared from ethyl sodio-3-oxobutanoate and acetyl chloride.[8] The other 1,3-diketones (**2a**—**c**, **e**—**g**) were purchased from Tokyo-Kasei Co., Ltd. and used as received.

Reaction of Alkenes with 1,3-Diketones (2a—h) in the Presence of Metal Acetate-O₂. The general procedure for the reaction of alkenes with 1,3-diketones in the presence of a metal acetate was as follows. A metal acetate (1 mmol) was added to a stirred solution of an alkene (1 mmol) and a 1,3-diketone (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 under a dry-air stream for the period of time shown in Tables 1 and 2. The reaction was quenched by adding water (60 cm^3); the mixture was then extracted with benzene. After removing the benzene, the resulting products were separated either on TLC (Wakogel B10) while eluting with chloroform or on a silica-gel column while eluting with benzene. The products were further purified by recrystallization from appropriate solvents. The yields are listed in Tables 1 and 2.

Products. 1-Hydroxy-6-methyl-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-7-one (3aa): Mp 115—116 °C (from methanol-water); IR (KBr) ν=3480 (-OH) and 1701 (>C=O); ^1H NMR (DMSO-d_6) δ=0.98 (3H, s, CH_3), 1.31—2.56 (6H, m, $-(CH_2)_3-$), 2.49 (1H, d, J=14 Hz, $-\underline{H}CH-$) and 3.27 (1H, d, J=14 Hz, $-HC\underline{H}-$), 6.71 (1H, s, -OH), and 7.01—7.74 (10H, m, 2×Ph); Found: C, 74.53; H, 6.55%. Calcd for $C_{21}H_{22}O_4$: C, 74.69; H, 6.72%.

1-Hydroxy-6-methyl-4,4-diphenyl-2,3-dioxabicyclo[4.3.0]nonan-7-one (3ab): Mp 171—172 °C (from methanol); IR (KBr) ν=3384 (-OH) and 1731 (>C=O); ^1H NMR ($CDCl_3$) δ=1.06 (3H, s, CH_3), 1.40—2.43 (4H, m, $-(CH_2)_2-$), 2.32 (1H, d, J=14 Hz, $-\underline{H}CH-$) and 3.28 (1H, d, J=14 Hz, $-HC\underline{H}-$), 3.62

(1H, s, -OH), and 7.08—7.73 (10H, m, 2×Ph); ^{13}C NMR (DMSO-d_6) δ=216.08 (>C=O), 144.734 (=C<), 141.327 (=C<), 128.156 (=CH-), 128.110 (=CH-), 127.289 (=CH-), 127.051 (=CH-), 126.454 (=CH-), 125.096 (=CH-), 106.062 (C-1), 84.088 (C-4), 48.301 (C-6), 36.144 (C-8), 36.084 (C-10), 29.010 (C-9), and 21.092 (CH$_3$); Found: C, 73.85; H, 6.36%. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22%.

6-Acetyl-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-1-ol (3ac): Mp 156—157 °C (from methanol-water); IR (KBr) ν=3304 (-OH) and 1678 (>C=O); ^{1}H NMR (CDCl$_3$) δ=1.18—2.21 (8H, m, -(CH$_2$)$_4$-), 2.02 (3H, s, CH$_3$), 2.88 (2H, s, -CH$_2$-), 5.33 (1H, br, -OH), and 7.13—7.67 (10H, m, 2×Ph); Found: C, 74.86; H, 7.02%. Calcd for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86%.

4-Ethoxycarbonyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ad): Mp 144—146 °C (from benzene-hexane).[2a)]

4-Acetyl-3,4-dimethyl-6,6-diphenyl-1,2-dioxan-3-ol (3ae): Mp 147.8 °C (lit,[2b)] 147.8 °C).

1-Hydroxy-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-7-one (3af): Mp 184—186 °C (lit,[2b)] mp 184—186 °C).

4,4-Bis(4-chlorophenyl)-1-hydroxy-6-methyl-2,3-dioxa[4.4.0]decan-7-one (3ba): Mp 177—178 °C (from methanol-water); IR (KBr) ν=3502 (OH) and 1703 (>C=O); ^{1}H NMR (DMSO-d_6) δ=1.03 (3H, s, -CH$_3$), 1.22—2.23 (6H, m, -(CH$_2$)$_3$-), 2.42 (1H, d, J=12.0 Hz, -$\underline{H}$CH-), 3.29 (1H, d, J=12.0 Hz, -HC$\underline{H}$-), 6.81 (1H, s, OH), and 7.33—7.57 (8H, m, arom. H); Found: C, 61.91; H, 4.99%. Calcd for $C_{21}H_{20}Cl_2O_4$: C, 61.98; H, 4.95%.

4,4′-Dichlorobenzophenone (4b): Mp 145—146 °C.

4,4-Bis(4-methoxyphenyl)-1-hydroxy-6-methyl-2,3-dioxa[4.4.0]decan-7-one (3da): Mp 165—167 °C (from benzene-hexane); IR (KBr) ν=3508 (OH) and 1701 (>C=O); ^{1}H NMR (CDCl$_3$) δ=1.22 (3H, s, CH$_3$), 1.24—2.27 (6H, m, -(CH$_2$)$_3$-), 2.45 (1H, d, J=12 Hz, -$\underline{H}$CH-), 3.42 (1H, d, J=12 Hz, -HC$\underline{H}$-), 3.67 (3H, s, OCH$_3$), 3.68 (3H, s, OCH$_3$), 4.85 (1H, s, OH), and 6.67—7.60 (8H, m, arom. H); Found: C, 69.15; H, 6.70%. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58%.

4,4′-Dimethoxybenzophenone (4d): Mp 140—141 °C.

4-Acetyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ag): Mp 165—166 °C (lit,[2b)] mp 165—166 °C).

4-Acetyl-6,6-bis(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (3bg): Mp 164—165 °C (lit,[2b)] mp 164—165 °C).

4-Acetyl-6,6-bis(4-methylphenyl)-3-methyl-1,2-dioxan-3-ol (3cg): Mp 138—139 °C (lit,[2b)] mp 138—139 °C).

2,2,9,9-Tetraphenyloctahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diol (5ah): Mp 183—184 °C (from benzene-hexane); IR (KBr) ν=3568-3404 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.80 (4H, s, -(CH$_2$)$_2$-), 2.63 (4H, s, 2×CH$_2$), 2.81 (2H, br, 2×OH), and 7.07—7.58 (20H, m, 4×Ph); ^{13}C NMR (CDCl$_3$) δ=145.610 (>C=), 144.968 (>C=), 128.514 (-CH=), 128.320 (-CH=), 127.291 (-CH=), 126.814 (-CH=), 125.382 (-CH=), 124.889 (-CH=), 108.863 (>C<), 83.642 (>C<), 48.020 (>C<), 40.591 (-CH$_2$-), and 32.550 (-CH$_2$-); Found: C, 76.13; H, 5.86%. Calcd for $C_{33}H_{30}O_6$: C, 75.84; H, 5.79%.

2,2,9,9-Tetrakis(4-chlorophenyl)octahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diol (5bh): Mp 188—189 °C (from benzene-hexane); IR (KBr) ν=3516-3403 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.85 (4H, s, -(CH$_2$)$_2$-), 2.60 (4H, s, 2×CH$_2$), 2.79 (2H, br, 2×OH), and 6.98—7.48 (16H, m, arom. H); Found: C, 60.53; H, 3.89%. Calcd for $C_{33}H_{26}Cl_4O_6$: C, 60.02; H, 3.93%.

2,2,9,9-Tetrakis(4-methylphenyl)octahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diol (5ch): Mp 206—207 °C (from benzene-hexane); IR (KBr) ν=3532-3460 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.87 (4H, s, -(CH$_2$)$_2$-), 2.28 (6H, s, 2×CH$_3$), 2.33 (6H, s, 2×CH$_3$), 2.65 (4H, s, 2×CH$_2$), 2.80 (2H, br, 2×OH), and 7.03—7.61 (16H, m, arom. H); ^{13}C NMR (CDCl$_3$) δ=142.801 (>C=), 142.234 (>C=), 136.864 (>C=), 136.372 (>C=), 129.047 (=CH-), 125.213 (=CH-), 124.781 (=CH-), 108.864 (>C<), 83.474 (>C<), 48.045 (>C<), 40.452 (-CH$_2$-), 32.471 (-CH$_2$-), and 20.910 (CH$_3$); Found: C, 77.10: H, 6.67%. Calcd for $C_{37}H_{38}O_6$: C, 76.80; H, 6.62%.

2,2,9,9-Tetrakis(4-methoxyphenyl)octahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diol (5dh): Mp 133—135 °C (from benzene-hexane); IR (KBr) ν=3600—3200 (-OH); ^{1}H NMR (CDCl$_3$), δ=1.85 (4H, s, -(CH$_2$)$_2$-), 2.62 (4H, s, 2×CH$_2$), 3.03 (2H, br. s, 2×OH), 3.72 (6H, s, 2×OCH$_3$), 3.78 (6H, s, 2×OCH$_3$), and 6.53—7.50 (16H, m, arom. H); Found: C, 69.03; H, 6.03%. Calcd for $C_{37}H_{38}O_{10}$: C, 69.14; H, 5.96%.

2,2,9,9-Tetrakis(4-fluorophenyl)octahydro-3,4,7,8-tetraoxabenz[*c*]indene-4a,6a-diol (5eh): Mp 164—166 °C (from benzene-hexane); IR (KBr) ν=3588—3476 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.82 (4H, s, -(CH$_2$)$_2$-), 2.68 (4H, s, 2×CH$_2$), 3.66 (2H, br, 2×OH), and 6.87—7.73 (16H, m, arom. H); Found: C, 66.91; H, 4.28%. Calcd for $C_{33}H_{26}F_4O_6$: C, 66.66; H, 4.40%.

Decomposition of 3ag—cg with Potassium Hydroxide in Methanol. A mixture of 3 (1 mmol) and 5% KOH-MeOH (10 cm^3) was heated under reflux for the period of time shown in Table 3. After cooling, 2 M (1 M=1 mol dm^{-3}) hydrochloric acid (20 cm^3) was added to the reaction mixture, the mixture was extracted with benzene (total 60 cm^3). After removing the benzene, the resulting mixture was chromatographed on a silica-gel plate while eluting with benzene. The yields are listed in Table 3.

Benzophenone (4a): Mp 47—49 °C.

4,4′-Dichlorobenzophenone (4b): Mp 145—146 °C.

4,4′-Dimethylbenzophenone (4c): Mp 92—94 °C.

3-Methyl-6,6-diphenyl-1,2-dioxan-3-ol (6a): Mp 137—140 °C (from benzene-hexane); IR (CHCl$_3$) ν=3604—3072 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.30 (3H, s, CH$_3$), 1.66—1.97 (2H, m, -C$\underline{H}_2$CH$_2$-), 2.48—2.80 (2H, m, -CH$_2$C$\underline{H}_2$-), 3.28 (1H, s, -OH), and 6.83—7.68 (10H, m, 2×Ph); Found: C, 75.66; H, 6.73%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

6,6-Bis(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (6b): Mp 102—103 °C (from ethanol-water); IR ν=3648-3164 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.28 (3H, s, CH$_3$), 1.58—1.93 (2H, m, -C$\underline{H}_2$CH$_2$-), 2.42—2.73 (2H, m, -CH$_2$C$\underline{H}_2$-), 3.53 (1H, s, -OH) and 7.16—7.52 (8H, m, arom. H); Found: C, 59.94; H, 4.79%. Calcd for $C_{17}H_{16}Cl_2O_3$: C, 60.19; H, 4.72%.

6,6-Bis(4-methylphenyl)-3-methyl-1,2-dioxan-3-ol (6c): Mp 60—61 °C (from hexane); IR (CHCl$_3$) ν=3684—3012 (-OH); ^{1}H NMR (CDCl$_3$) δ=1.27 (3H, s, CH$_3$), 1.68—2.03 (2H, m, -C$\underline{H}_2$CH$_2$-), 2.23 (3H, s, CH$_3$), 2.31 (3H, s, CH$_3$), 2.51—2.84 (2H, m, -CH$_2$C$\underline{H}_2$-), 3.72 (1H, s, -OH), and 7.12—7.65 (8H, m, arom. H); Found: C, 76.09; H, 7.66%. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%.

Decomposition of 3ag—cg with Hydrochloric Acid in Acetic Acid. A mixture of 3 (1 mmol) and 2 M hydrochloric acid (15 cm^3) in acetic acid (20 cm^3) was heated at 100 °C with stirring for 10—15 min. After adding water (20 cm^3) the mixture was extracted with diethyl ether (total 60 cm^3). After removing the ether, the resulting mixture was chromatographed on a silica-gel plate while eluting with a mixture of benzene and diethyl ether. The yields are listed in Table 4.

3-Acetyl-2-methyl-5-phenylfuran (7a):[9)] Mp 50—51 °C (from hexane); IR (KBr) ν=1671 (>C=O); ^{1}H NMR (CDCl$_3$)

δ=2.37 (3H, s, CH_3), 2.42 (3H, s, $-COCH_3$), 6.80 (1H, s, =CH–), and 7.06—7.72 (5H, m, Ph); Found: C, 77.58, H, 6.03%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

3-Acetyl-5-(4-chlorophenyl)-2-methylfuran (7b): Mp 112—114 °C (from hexane); IR (KBr) ν=1675 (>C=O); ^{1}H NMR ($CDCl_3$), δ=2.45 (3H, s, CH_3), 2.66 (3H, s, $-COCH_3$), 6.88 (1H, s, =CH–), 7.38 (2H, m, arom. H), and 7.63 (2H, m, arom. H); Found: C, 66.55; H, 4.76%. Calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.69%.

3-Acetyl-5-(4-methylphenyl)-2-methylfuran (7c): Mp 61—63 °C (from hexane), IR (KBr) ν=1672 (>C=O); ^{1}H NMR ($CDCl_3$) δ=2.33 (3H, s, CH_3), 2.41 (3H, s, $-COCH_3$), 2.62 (3H, s, $-C_6H_4C\underline{H}_3$), 6.75 (1H, s, =CH–), 7.17 (2H, m, arom. H), and 7.32 (2H, m, arom. H); Found: C, 78.33; H, 6.65%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

Phenol (8a): Mp 40—41 °C.

4-Chlorophenol (8b): Mp 42—43 °C.

4-Methylphenol (8c): Mp 31—33 °C.

1-Phenyl-1,4-pentanedione (9a): Bp 117 °C/66.8 Pa (lit,[10] bp 93—94 °C/13.3 Pa); IR ($CHCl_3$) ν=1714 (>C=O) and 1686 (>C=O); ^{1}H NMR ($CDCl_3$) δ=2.23 (3H, s, CH_3), 2.67—3.01 (2H, m, $-C\underline{H}_2CH_2-$), 3.10—3.42 (2H, m, $-CH_2C\underline{H}_2-$), and 7.33—8.12 (5H, m, Ph).

1-(4-Chlorphenyl)-1,4-pentanedione (9b): Mp 74—75 °C (lit,[10] mp 76 °C) (from benzene–hexane); IR ($CHCl_3$) ν=1717 (>C=O) and 1686 (>C=O); ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s, CH_3), 2.68—3.03 (2H, m, $-C\underline{H}_2CH_2-$), 3.11—3.43 (2H, m, $-CH_2C\underline{H}_2-$), 7.39 (2H, m, arom. H) and 7.93 (2H, m, arom. H).

1-(4-Methylphenyl)-1,4-pentanedione (9c): Mp 51—52 °C (lit,[11] mp 53 °C) (from benzene–hexane); IR ($CHCl_3$) ν=1716 (>C=O) and 1687 (>C=O); ^{1}H NMR (CCl_4) δ=2.13 (3H, s, CH_3), 2.35 (3H, s, $-C_6H_4C\underline{H}_3$), 2.53—2.83 (2H, m, $-C\underline{H}_2CH_2-$), 2.93—3.23 (2H, m, $-CH_2C\underline{H}_2-$), 7.16 (2H, m, arom. H) and 7.83 (2H, m, arom. H).

Decomposition of 6a—c with Hydrochloric Acid in Acetic Acid. Compound **6** (0.50 mmol) was dissolved in a mixed solution of 2 M hydrochloric acid (5 cm^3) and acetic acid (10 cm^3). The solution was kept at 80 °C on a thermostated oil bath with stirring for 20 min. After adding water (20 cm^3) the mixture was extracted with diethyl ether (total 60 cm^3). After removing ether, the resulting mixture was chromatographed on a silica-gel plate while eluting with a mixture of benzene and diethyl ether. The yields of **8a**—**c** and **9a**—**c** are listed in Table 4.

MM2 Calculations. In order to determine the relative stabilities of the possible structural isomers, MM2 calculations for compounds **3ac** and **3ac′** were performed by Chem 3D Plus (Version 3.0) using standard measurements. By considering an anomeric effect for the 1,2-dioxan-3-ols ring, only the conformations which might have the lowest energy were calculated. The results were as follows: *trans*-**3ac** (26.5 kcal mol^{-1}), *cis*-**3ac** (a(Ac), e(OH); 31.3 kcal mol^{-1}), *cis*-**3ac** (a(OH), e(Ac); 26.4 kcal mol^{-1}), (*Z*)-**3ac′** (a(OH), e(>C=O); 31.8 kcal mol^{-1}), (*Z*)-**3ac′** (e(OH), a(>C=O); 29.3 kcal mol), (*E*)-**3ac′** (a(OH), a(>C=O); 31.7 kcal mol^{-1}), (*E*)-**3ac′** (e(OH), e(>C=O); 27.6 kcal mol^{-1}).

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