

Reactions of 1,1-Disubstituted Alkenes with Acetoacetamides and Molecular Oxygen in the Presence of Manganese(III) Acetate

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The reactions of 1,1-disubstituted ethenes with acetoacetamide or *N*-substituted acetoacetamides, and molecular oxygen in the presence of manganese(III) acetate gave a mixture of *c*-4- and *t*-4-carbamoyl-3-methyl-1,2-dioxan-*r*-3-ols in good yields. Effects of substituents in the alkenes as well as in the carbamoyl group in the acetoacetamides were observed. Stereochemistry and the reactivity of the 4-carbamoyl-3-methyl-1,2-dioxan-3-ols are discussed.

A number of cyclic peroxides having a 1,2-dioxane ring system have been isolated from natural sources and have some biological activities.¹⁾ We recently reported that the manganese(III)-based oxidative free-radical cyclization of alkenes with 1,3-dicarbonyl compounds and molecular oxygen produced 4-acyl-1,2-dioxan-3-ols in moderate to good yields.²⁾ Since the reaction is extremely facile for the synthesis of 1,2-dioxan-3-ols and the products may have some biological activities, we have investigated the reaction of alkenes with acetoacetamides in the presence of manganese(III) acetate (abbreviated [Mn(OAc)₃]) and molecular oxygen (O₂).

Results and Discussion

The reactions were carried out at various molar ratios of alkene : acetoacetamide : [Mn(OAc)₃]. When a mixture of 1,1-diphenylethene (**1a**), *N*-(4-methylphenyl)-acetoacetamide (**2a**), and [Mn(OAc)₃] was stirred in acetic acid under a current of dried air at 23 °C, the product was found to be 4-(4-methylphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3aa**). The structure of **3aa** was elucidated by ¹H and ¹³C NMR, IR spectra, and elemental analysis (Fig. 1). The maximum yield for **3aa** was attained from the reaction with a molar ratio of 1 : 3 : 1 (Table 1, Entry 3). The yield of **3aa** decreased when the reaction was carried out using a small volume of acetic acid (Entry 5). The reaction under an atmosphere of O₂ gave a slightly decreased yield (Entry 6). The reaction under an atmosphere of argon gave 3-(4-methylphenylcarbamoyl)-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**4aa**) along with a large amount of unchanged alkene (Entry 7). The reactions at a slightly higher or lower temperature resulted in decreased yields of **3aa** (Entries 8, 9). Benzophenone was formed in the reaction at a higher temperature. Addition of water and the use of propanoic acid as a solvent also lowered the yield (Entries 10, 12), but the reactions in the presence of acetic anhydride and potassium acetate gave **3aa** in good yields (Entries 13, 14). Other metal acetates, such as Co(II), Co(III), Mn(II), Cu(II), Ni(II), Tl(III), Pb(IV), and FeCl₃ were used and it was found that similar reactions at 23 °C for 12–14 h in the presence of Co(II), Co(III), or Mn(II) did yield 4-

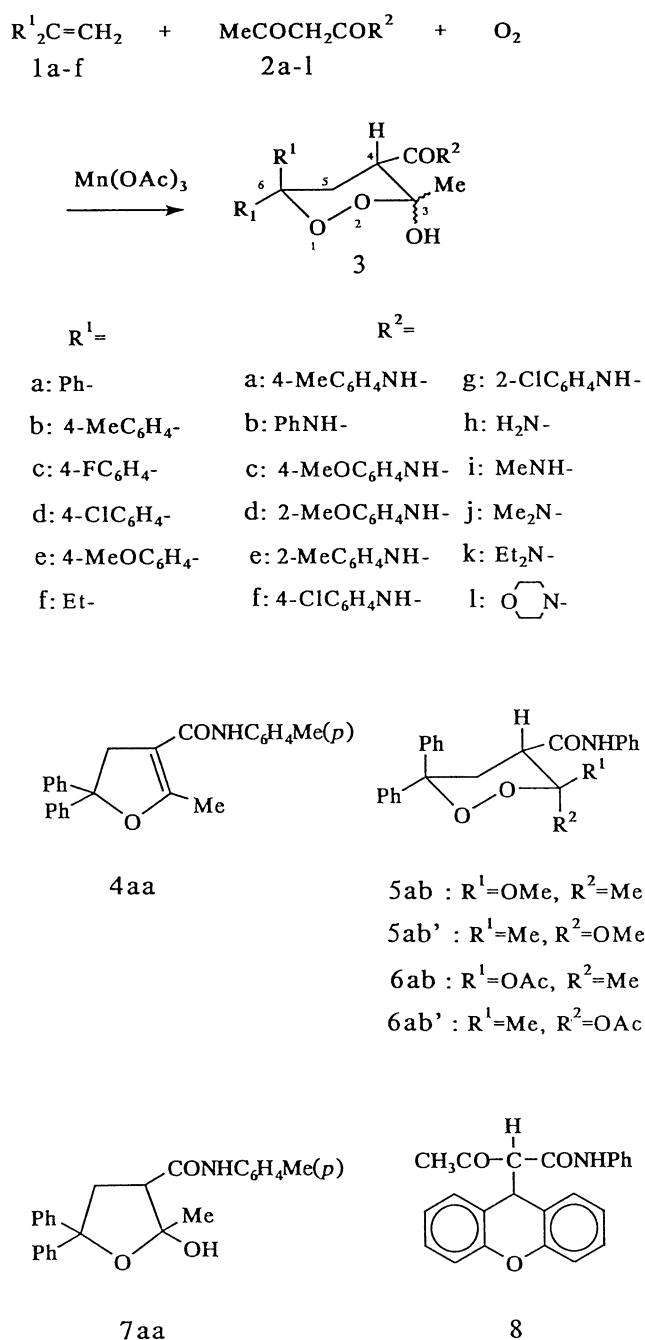


Fig. 1.

Table 1. Reactions of 1,1-Diphenylethene (**1a**) with *N*-(4-Methylphenyl)acetoacetamide (**2a**) and [Mn(OAc)₃]-O₂

Entry	Molar ratio ^{a)}	Solvent ^{b)}	Temp	Time	Product composition (yield/%) ^{c)}		
			°C	h	1a	3aa	4aa
1	1:1:1	AcOH	23	14		61	
2	1:2:1	AcOH	23	14		81	
3	1:3:1	AcOH	23	13		92	
4	1:3:1	AcOH ^{d)}	23	13		89	
5	1:3:1	AcOH ^{e)}	23	14		58	
6	1:3:1	AcOH ^{f)}	23	14		78	
7	1:3:1	AcOH ^{g)}	23	14	62		29
8	1:3:1	AcOH	36—42	6		34	18 ^{h)}
9	1:3:1	AcOH	15—18	15		55	
10	1:3:1	AcOH-H ₂ O ⁱ⁾	23	14		58	
11	1:3:1	HCOOH	23	16	100		
12	1:3:1	C ₂ H ₅ CO ₂ H	23	14		51	33
13	1:3:1	AcOH-Ac ₂ O ^{j)}	23	13		80	
14	1:3:1	AcOH-AcOK ^{k)}	23	13		93	

a) **1a**:**2a**: [Mn(OAc)₃]. b) 25 cm³ of solvent was used unless otherwise stated. c) Isolated yields (calculated on the basis of the alkene added). d) Acetic acid (60 cm³) was used. e) Acetic acid (10 cm³) was used. f) The reaction was carried out under an oxygen atmosphere. g) The reaction was carried out under an argon atmosphere and **2a** was recovered (59% yield). h) Benzophenone was obtained (5% yield). i) Water (7.5 cm³) was added. j) Acetic anhydride (500 mg) was added. k) Potassium acetate (100 mg) was added.

Table 2. Reactions of 1,1-Disubstituted Ethenes (**1a—f**) with Acetoacetamides (**2a—l**) and [Mn(OAc)₃]-O₂^{a)}

Entry	Alkene	Acetoacetamide	Time	Product (Yield/%) ^{b)}	Isomer ratio
			h		
15	1a	2a	13	3aa (92)	59:41
16	1a	2b	12	3ab (96)	62:38
17	1a	2c	14	3ac (82)	63:36
18	1a	2d	14	3ad (84)	73:27
19	1a	2e	12	3ae (94)	83:17
20	1a	2f	12	3af (94)	57:43
21	1a	2g	12	3ag (93)	74:26
22	1a	2h	12	3ah (88)	56:44
23	1a	2i	13	3ai (85)	58:42
24	1a	2j	12	3aj (87)	95: 5
25	1a	2k	12	3ak (89)	96: 4
26	1a	2l	11	3al (88)	100: 0
27	1b	2a	13	3ba (99)	54:46
28	1b	2b	12	3bb (98)	56:44
29	1b	2e	12	3be (100)	77:23
30	1b	2f	14	3bf (99)	67:33
31	1b	2g	12	3bg (100)	94: 6
32	1b	2h	13	3bh (96)	59:41
33	1c	2b	12	3cb (94)	53:47
34	1c	2j	13	3cj (59)	94: 6
35	1d	2g	14	3dg (87)	91: 9
36	1d	2j	12	3dj (89)	94: 6
37	1e	2g	13	3eg (83)	91: 9
38	1e	2j	12	3ej (78)	96: 4
39	1f	2b	12	3fb (68)	56:44
40	1f	2f	12	3ff (62)	54:46

a) The reactions were carried out in acetic acid at a 1:3:1 molar ratio for alkene: acetoacetamide: [Mn(OAc)₃] at 23 °C under a current of air. b) Isolated yield (calculated on the basis of alkene used).

(4-methylphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3aa**) (Co(II), 60% yield; Co(III), 66% yield; Mn(II), 92% yield). It was thus shown that Mn(II) was

as effective as Mn(III).

The reactions of 1,1-bis(4-methylphenyl)ethene (**1b**), 1,1-bis(4-fluorophenyl)ethene (**1c**), 1,1-bis(4-chloro-

phenyl)ethene (**1d**), 1,1-(4-methoxyphenyl)ethene (**1e**), and 2-ethyl-1-butene (**1f**) using acetoacetamide (**2h**) and various *N*-substituted acetoacetamides: *N*-phenyl- (**2b**), *N*-(4-methoxyphenyl)- (**2c**), *N*-(2-methoxyphenyl)- (**2d**), *N*-(2-methylphenyl)- (**2e**), *N*-(4-chlorophenyl)- (**2f**), *N*-(2-chlorophenyl)- (**2g**), *N*-methyl- (**2i**), *N,N*-dimethyl- (**2j**) and *N,N*-diethylacetoacetamide (**2k**), and *N*-(1,3-dioxobutyl)morpholine (**2l**) were then examined. The reactions were carried out in acetic acid with [Mn(OAc)₃] at a molar ratio of 1 : 3 : 1 at 23 °C under an air stream. The results are listed in Table 2. 1,1-Diphenylethenes (**1a**—**e**) always gave 4-carbamoyl-3-methyl-1,2-dioxan-3-ols in excellent yields, whereas 2-ethyl-1-butene (**1f**) yielded the corresponding 4-carbamoyl-3-methyl-1,2-dioxan-3-ols in a slightly lower yield (Entries 39, 40). (*E*)-1,2-Diphenylethene and triphenylethene were not reactive.

Structural Assignments. Contrary to the reactions of the 1,3-diketones which gave a single stereoisomer,²⁾ the reaction of acetoacetamides yielded a mixture of two stereoisomers. When recrystallized **3ab** was dissolved in DMSO-*d*₆ for measurement of the ¹H NMR spectra, two methyl proton signals appeared at δ=1.27 and 1.53. The intensity of the methyl signal at the lower field gradually increased, while that of the methyl signal at the higher field decreased. The change in the intensities was followed at intervals and it was found that the mixture reached equilibrium after 12 h at room temperature. Thus, each isomer ratio (shown in Table 2) was determined from the intensities of the two methyl signals in the ¹H NMR spectrum at 12 h after preparing the solution. The ¹³C NMR spectrum in DMSO-*d*₆ exhibited a pair of carbon signals: carbonyl carbons at δ=168.879 and 168.640, carbons attached to two oxygens at δ=101.885 and 98.185, carbons attached to one oxygen at δ=84.894 and 84.416, methine carbons at δ=48.212 and 47.391, methylene carbons at δ=34.234 and 30.624, and methyl carbons at δ=24.239 and 20.063. The assignments were based on their DEPT-135 and -90 spectra. The methyl ¹H signals at δ=1.27 and 1.53 were correlated to the methyl carbon signals at δ=24.239 and 20.063, respectively, by measuring a H,C COSY spectrum. The difference of the chemical shifts for the methyl signals in the ¹³C NMR spectrum would

indicate the different conformations of these methyl groups at the C-3 position in a 1,2-dioxane ring, that is, axial and equatorial methyl groups. In order to clarify the matter, methyl and acetyl derivatives of **3ab** were prepared and their ¹³C NMR spectra were analyzed (Table 3). Treatment of **3ab** with dimethyl sulfate and potassium carbonate in refluxing acetone yielded two isomeric methyl derivatives, **5ab** (49%) and **5ab'** (35%) which were separated on a silica-gel column. It was the methyl carbon at the C-3 position that showed a larger chemical-shift difference than others in the ¹³C NMR spectrum, and it appeared at δ=18.918 for **5ab** and δ=14.545 for **5ab'** (Table 3). It has been assigned that the methyl carbon with the higher field shift had an axial conformation, and the one with the lower field shift had an equatorial conformation.³⁾ A -CH₂-CH< unit in **5ab** and **5ab'** was shown as an ABX and an AB₂ spin system, respectively, in the 400 MHz ¹H NMR spectra. Since both spin systems had large *J* values: *J*_{AB}=13.20, *J*_{AX}=14.83, *J*_{BX}=4.57 Hz for **5ab** and *J*_{AB}=13.9 Hz for **5ab'**, H-4 should have had a large *J* value as an axial hydrogen. It followed that both carbamoyl groups at C-4 in **5ab** and **5ab'** could be assigned as equatorial. Thus, the structures of **5ab** and **5ab'** were shown to be *c*-4-(phenylcarbamoyl)-*r*-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane and *t*-4-(phenylcarbamoyl)-*r*-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane, respectively (Fig. 1).

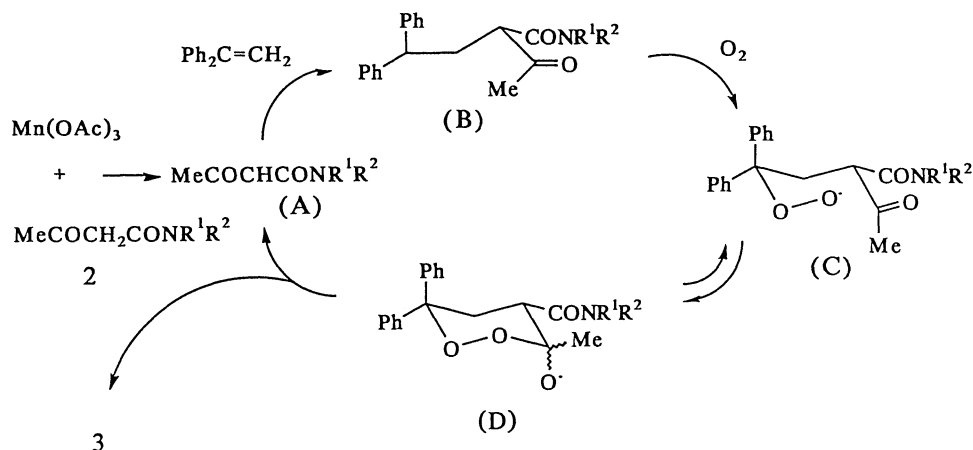
A similar situation existed for the acetates of **3ab**, which again consisted of two isomers, **6ab**, (54%) and **6ab'** (21%). The methyl carbon at C-3 appeared at δ=21.332 for **6ab** and δ=17.424 for **6ab'** (Table 3). Therefore, the structures of *c*-4-(phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-*r*-3-ol acetate and *t*-4-(phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-*r*-3-ol acetate could be assigned to **6ab** and **6ab'**, respectively.

It was thus shown that 4-(phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ols (**3ab**) exist as an equilibrium mixture of two epimers at the C-3 position. This made quite a contrast with the 4-acetyl-3-methyl-1,2-dioxan-3-ols which were shown to exist as a single stereoisomer having an axial hydroxyl group.²⁾ It seems possible that hydrogen bonds can be formed

Table 3. Spectral Data for 4-(Phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3ab**) and Its Derivatives

Compound	¹³ C NMR (δ)								¹ H NMR (δ)		IR(ν)	
	>C=O	C-3	C-4	C-5	C-6	Me	OMe	OAc	Me	>C=O, -OAc		
3ab	168.640	98.185	47.391	30.624	84.416	20.063 (a) ^{a)}			1.53 (a)	1657		
	168.879	101.885	48.212	34.234	84.896	24.239 (e) ^{b)}			1.27 (e)			
5ab	169.316	100.860	50.439	33.806	85.704	18.918 (e)	49.350		1.30 (e)	1664		
5ab'	168.463	106.556	48.243	32.863	87.208	14.545 (a)	50.018		1.34 (a)	1692		
6ab	167.538	103.259	50.555	32.833	85.790	21.332 (e)		22.212	1.70 (e)	1665	1731	
	167.448											
6ab'	168.386	109.047	48.362	32.953	86.939	17.424 (a)		22.257	1.73 (a)	1690	1732	
	167.657											

a) a: axial. b) e: equatorial.



Scheme 1. The reaction mechanisms.

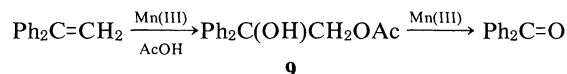
between the hydroxyl and carbamoyl groups in **3ab** irrespective of the conformation of the hydroxyl group, either axial or equatorial, and this could make the stability of the epimers comparable. **3ab** exhibited carbonyl absorption at ν 1657 which was compared with **5ab** (ν 1664), **5ab'** (ν 1692), **6ab** (ν 1665), and **6ab'** (ν 1690) (Table 3). This indicated the presence of hydrogen bonding between the hydroxyl and carbamoyl groups in **3ab**. On the other hand, the hydrogen bonding between the hydroxyl group and the carbonyl function in 4-acetyl-3-methyl-1,2-dioxan-3-ols may be weak, since the carbonyl absorption of this compound appeared at ν 1696 while that of the acetate appeared at ν 1701.²⁾ Therefore, the conformation of the hydroxyl group in 4-acetyl-3-methyl-1,2-dioxan-3-ol would be controlled mainly by an anomeric effect.⁴⁾

Reactions of 3aa. Compound **3aa** was hydrogenated in the presence of palladium on charcoal as catalyst in ethanol to give 3-(4-methylphenylcarbamoyl)-2-methyl-5,5-diphenyl-tetrahydro-2-furanol (**7aa**), while hydrogenation in acetic acid yielded **4aa**, which was identical with that obtained in the manganese(III) acetate oxidation under an atmosphere of argon. On heating in acetic acid, **7aa** gave **4aa**. Treatment of **3aa** with aqueous potassium hydroxide solution yielded benzophenone in a moderate yield.

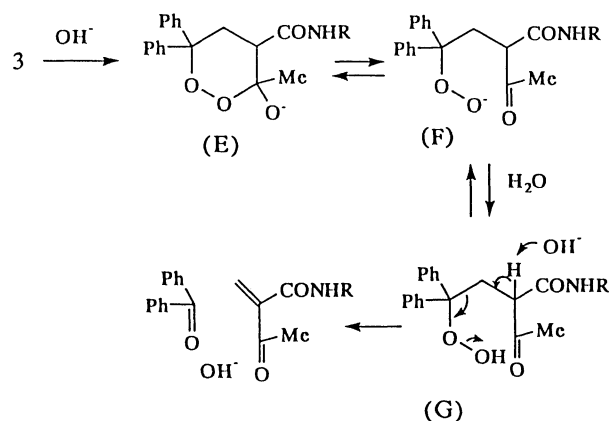
Reaction Mechanisms for the Formation of Compounds 3. The reaction could be accounted for in terms of a radical reaction initiated by the acetylcarbamoylmethyl radical (A), $\cdot\text{CH}(\text{COCH}_3)\text{CONR}^1\text{R}^2$, that was formed either by the interaction of $[\text{Mn}(\text{OAc})_3]$ with acetoacetamide (**2**) or by the reaction of **2** with a carboxymethyl radical, $\cdot\text{CH}_2\text{CO}_2\text{H}$, which could be produced by the thermal decomposition⁵⁾ of $[\text{Mn}(\text{OAc})_3]$. However, it seemed unlikely that the carboxymethyl radical would be formed at room temperature. Although we have not succeeded in obtaining a stable Mn(III)-acetoacetamide complex, the radical A could be produced by the interaction of **2** with $[\text{Mn}(\text{OAc})_3]$. In fact, the radical A was trapped with xanthene to give *N*-phenyl-

2-(9-xanthenyl)acetoacetamide (**8**) as in the reaction of malonamide.⁶⁾ The radical A attacked an alkene forming a stable tertiary carbon radical (B) which reacted with molecular oxygen to form a peroxy radical (C), and then the alkoxy radical (D), and finally gave **3** (Scheme 1). The reaction of B under an atmosphere of argon or reaction at an elevated temperature yielded the dihydrofuran (**4ab**).

Benzophenone was obtained in a reaction at a slightly higher temperature. The reaction of **1a** with $[\text{Mn}(\text{OAc})_3]$ in the absence of acetoacetamide yielded 2,2-diphenyl-2-hydroxyethyl acetate (**9**) (4% yield) and benzophenone (7% yield). Thus, the formation of benzophenone could be envisaged as follows:



Alkaline degradation of **3aa** yielded benzophenone and a polymeric product which exhibited a broad multiplet at $\delta=3.7$ together with other signals at $\delta=7.3$ and 2.2. This could be explained as follows: a hydroxide ion attacked the proton on the C₍₃₎-OH to give an alkoxide anion (E), in which the 1,2-dioxane ring was



Scheme 2. R=4-methylphenyl.

opened to yield a peroxide anion (**F**). Abstraction of a proton from a solvent molecule and further decomposition of **G** yielded benzophenone and an acrylamide. The latter could not be isolated probably because of polymerization (Scheme 2).

It could thus be concluded that the facile radical reaction of an acetylcarbamoylmethyl radical with an alkene and molecular oxygen yielded a mixture of *c*-4- and *t*-4-carbamoyl-3-methyl-1,2-dioxan-*r*-3-ols (**3**) in excellent yields, although the electro-initiated formation of cyclic peroxide was reported.⁷⁾ The latter reaction seemed to be limited to the 1,3-dicarbonyl compounds which could produce only tertiary carbon radicals. Our reaction, on the other hand, has been successful with active methylenes as well as active methine compounds having an acyl and a carbamoyl group. This can be utilized in organic syntheses.

Experimental

Measurements. All the 1H and ^{13}C NMR spectra were taken either with JNM PMX-60SI (60 MHz), JNM EX-90 FT NMR (90 MHz for 1H , 22.4 MHz for ^{13}C) or JNM GX-400 FT NMR (400 MHz) 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. The IR data are expressed in cm^{-1} . All melting points were determined with a Yanaco MP-J3 micromelting point apparatus.

Materials. Manganese(III) acetate⁸⁾ was prepared according to the method 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.⁹⁾ 2-Ethyl-1-butene (**1f**) and the acetoacetamides (**2a**–**2l**) were purchased from Tokyo-Kasei Co., Ltd. and used as received.

Reaction of Alkenes with Acetoacetamide in the Presence of Manganese(III) Acetate- O_2 . The general procedure for the reaction of alkenes with acetoacetamide in the presence of $[Mn(OAc)_3]-O_2$ was as follows. $[Mn(OAc)_3]$ (1 mmol) was added to a stirred solution of an alkene (**1**, 1 mmol) and an acetoacetamide (**2**, 1–3 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 an air stream for the period of time shown in Tables 1 and 2. The solvent was removed in vacuo and the residue was triturated with water, followed by extraction with benzene. The products were separated either on TLC (Wakogel B10) while eluting with chloroform, or on a silica-gel column eluting with benzene. The products were further purified by recrystallization from appropriate solvents. The yields are listed in Tables 1 and 2.

Products. **4-(4-Methylphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3aa):** Mp 197–199 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1648; 1H NMR (60 MHz, DMSO- d_6) δ =1.23 and 1.47 (s, s, 3H), 2.22 (s, 3H), 2.71–3.02 (m, 3H), 6.83 and 7.01 (s, s, 1H), 7.05–7.81 (m, 14H), and 9.71 (br. s, 1H). Found: C, 74.38; H, 6.21; N, 3.51%. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47%.

4-(Phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ab): Mp 168–170 °C (from benzene–hexane); IR (KBr)

ν 3500–3100 and 1657; 1H NMR (60 MHz, DMSO- d_6) δ =1.27 and 1.53 (s, s, 3H), 2.70–3.01 (m, 3H), 6.72 and 7.03 (s, s, 1H), 7.06–7.77 (m, 15H), and 9.73 (br. s, 1H). Found: C, 74.04; H, 5.85; N, 3.57%. Calcd for $C_{24}H_{23}O_4N$: C, 74.02; H, 5.95; N, 3.60%.

4-(4-Methoxyphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ac): Mp 180–182 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1641; 1H NMR (60 MHz, DMSO- d_6) δ =1.23 and 1.50 (s, s, 3H), 2.60–3.01 (m, 3H), 3.69 (s, 3H), 6.75 and 6.93 (s, s, 1H), 7.15–7.71 (m, 14H), and 9.62 (br. s, 1H). Found: C, 71.98; H, 6.33; N, 3.13%. Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34%.

4-(2-Methoxyphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ad): Mp 188–190 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1640; 1H NMR (60 MHz, DMSO- d_6) δ =1.28 and 1.53 (s, s, 3H), 2.60–3.01 (m, 3H), 3.85 (s, 3H), 6.93 and 7.05 (s, s, 1H), 7.13–8.33 (m, 14H), and 9.67 (br. s, 1H). Found: C, 71.48; H, 6.27; N, 3.04%. Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34%.

4-(2-Methylphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ae): Mp 197–199 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1644; 1H NMR (60 MHz, DMSO- d_6) δ =1.34 and 1.57 (s, s, 3H), 2.23 (s, 3H), 2.70–3.01 (m, 3H), 7.01 and 7.32 (s, s, 1H), 7.68–7.90 (m, 14H), and 9.41 (br. s, 1H). Found: C, 74.62; H, 6.29; N, 3.43%. Calcd for $C_{25}H_{25}NO_4$: C, 74.42; H, 6.25; N, 3.47%.

4-(4-Chlorophenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3af): Mp 192–194 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1662; 1H NMR (60 MHz, DMSO- d_6) δ =1.29 and 1.51 (s, s, 3H), 2.70–3.01 (m, 3H), 6.86 and 7.18 (s, s, 1H), 7.30–7.74 (m, 14H), and 9.72 (br. s, 1H). Found: C, 68.07; H, 5.20; N, 3.34%. Calcd for $C_{24}H_{22}ClNO_4$: C, 68.00; H, 5.23; N, 3.30%.

4-(2-Chlorophenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ag): Mp 191–193 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1656; 1H NMR (60 MHz, DMSO- d_6) δ =1.36 and 1.52 (s, s, 3H), 2.80–3.13 (m, 3H), 7.03 and 7.16 (s, s, 1H), 7.31–7.76 (m, 14H), and 9.88 (br. s, 1H). Found: C, 67.78; H, 5.17; N, 3.30%. Calcd for $C_{24}H_{22}ClNO_4$: C, 68.00; H, 5.23; N, 3.30%.

4-Carbamoyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ah): Mp 179–181 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1659; 1H NMR (60 MHz, DMSO- d_6) δ =1.10 and 1.38 (s, s, 3H), 2.32–3.02 (m, 3H), 6.64 and 6.88 (s, s, 1H), 7.15 (br. s, 2H), and 7.17–7.73 (m, 10H). Found: C, 69.19; H, 6.09; N, 4.45%. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47%.

4-(Methylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ai): Mp 193–195 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1645; 1H NMR (60 MHz, DMSO- d_6) δ =1.17 and 1.45 (s, s, 3H), 2.62 and 2.68 (s, s, 3H), 2.27–3.05 (m, 3H), 6.67 and 6.85 (s, s, 1H), 6.95–7.67 (m, 10H), and 7.82 (br. s, 1H). Found: C, 69.67; H, 6.40; N, 4.33%. Calcd for $C_{19}H_{21}NO_4$: C, 69.70; H, 6.47; N, 4.28%.

c-4-(Dimethylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-*r*-3-ol (3aj): Mp 193–194 °C (from benzene–hexane); IR (KBr) ν 3260 and 1611; 1H NMR (60 MHz, DMSO- d_6) δ =1.07 (s, 3H), 2.88 (s, 3H), 2.97 (s, 3H), 2.63–3.13 (m, 3H), 6.78 (s, 1H), and 7.16–7.78 (m, 10H); ^{13}C NMR (DMSO- d_6) δ =172.086, 143.653, 141.714, 128.288, 128.154, 127.587, 127.080, 126.304, 125.350, 98.140, 84.103, 42.304, 39.787, 37.068, 31.370, and 24.970. Found: C, 70.41; H, 6.71; N, 4.16%. Calcd for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N,

4.10%.

***t*-4-(Dimethylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-*r*-3-ol (3aj):** Mp 190–191 °C (from benzene–hexane); IR (KBr) ν 3236 and 1614; ^1H NMR (60 MHz, DMSO- d_6) δ =1.38 (s, 3H), 2.91 (s, 3H), 3.01 (s, 3H), 2.65–3.15 (m, 3H), 6.87 (s, 1H), and 7.18–7.81 (m, 10H); ^{13}C NMR (DMSO- d_6) δ =170.202, 145.041, 142.132, 128.286, 128.169, 127.796, 127.080, 126.290, 125.171, 102.705, 84.924, 42.767, 37.334, 35.442, 35.442, and 20.286. Found: C, 70.38; H, 6.78; N, 4.11%. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_4$: C, 70.36; H, 6.79; N, 4.10%.

4-(Diethylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ak): Mp 190–191 °C (from benzene–hexane); IR (KBr) ν 3276 and 1613; ^1H NMR (60 MHz, DMSO- d_6) δ =0.81–1.23 (m, 6H), 1.06 and 1.23 (s, s, 3H), 2.63–2.96 (m, 3H), 3.05–3.53 (m, 4H), 6.78 and 6.97 (s, s, 1H), and 7.06–7.83 (m, 10H); ^{13}C NMR (DMSO- d_6) δ =171.445, 143.430, 141.610, 128.259, 128.140, 127.617, 127.065, 126.260, 125.410, 97.947, 84.163, 42.767, 41.917, 40.425, 32.026, 24.866, 14.439, and 12.738. Found: C, 71.59; H, 7.36; N, 3.86%. Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_4$: C, 71.52; H, 7.37; N, 3.79%.

4-(Morpholinocarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3al): Mp 196–197 °C (from benzene–hexane); IR (KBr) ν 3276 and 1612; ^1H NMR (60 MHz, DMSO- d_6) δ =1.33 (s, 3H), 2.61–3.11 (m, 3H), 3.12–4.01 (m, 8H), 7.03 (s, 1H), and 7.21–7.61 (m, 10H); ^{13}C NMR (DMSO- d_6) δ =168.714, 143.762, 141.982, 128.318, 128.184, 127.140, 127.095, 126.215, 125.171, 102.451, 85.043, 66.142, 46.138, 42.498, 42.051, 35.234, and 20.107. Found: C, 68.63; H, 6.58; N, 3.61%. Calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_5$: C, 68.91; H, 6.57; N, 3.65%.

6,6-Bis(4-methylphenyl)-4-(4-methylphenylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3ba): Mp 165–168 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1650; ^1H NMR (60 MHz, DMSO- d_6) δ =1.22 and 1.48 (s, s, 3H), 2.20 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.57–2.98 (m, 3H), 6.77 and 6.90 (s, s, 1H), 6.78–7.60 (m, 12H), and 9.62 (br. s, 1H). Found: C, 75.17; H, 6.77; N, 3.24%. Calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_4$: C, 75.15; H, 6.77; N, 3.25%.

6,6-Bis(4-methylphenyl)-4-(phenylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3bb): Mp 193–195 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1659; ^1H NMR (60 MHz, DMSO- d_6) δ =1.23 and 1.48 (s, s, 3H), 2.05 (s, 3H), 2.12 (s, 3H), 2.61–3.01 (m, 3H), 6.71 and 6.75 (s, s, 1H), 6.93–7.73 (m, 13H), and 9.83 (br. s, 1H). Found: C, 74.85; H, 6.51; N, 3.37%. Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_4$: C, 74.80; H, 6.52; N, 3.36%.

6,6-Bis(4-methylphenyl)-4-(2-methylphenylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3be): Mp 164–167 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1624; ^1H NMR (60 MHz, DMSO- d_6) δ =1.27 and 1.44 (s, s, 3H), 2.17 (s, 3H), 2.21 (s, 3H), 2.29 (s, 3H), 2.61–3.01 (m, 3H), 6.98 and 7.32 (s, 1H), 7.02–7.69 (m, 12H), and 9.28 (br. s, 1H). Found: C, 75.09; H, 6.78; N, 3.24%. Calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_4$: C, 75.15; H, 6.77; N, 3.25%.

4-(4-Chlorophenylcarbamoyl)-6,6-bis(4-methylphenyl)-3-methyl-1,2-dioxan-3-ol (3bf): Mp 120–123 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1658; ^1H NMR (60 MHz, DMSO- d_6) δ =1.25 and 1.52 (s, s, 3H), 2.18 (s, 3H), 2.29 (s, 3H), 2.63–3.01 (m, 3H), 6.72 and 7.00 (s, s, 1H), 7.03–7.92 (m, 12H), and 9.28 (br. s, 1H). Found: C, 68.83; H, 5.80; N, 3.17%. Calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}_4$: C, 69.10; H, 5.80; N, 3.10%.

4-(2-Chlorophenylcarbamoyl)-6,6-bis(4-methylphenyl)-3-

methyl-1,2-dioxan-3-ol (3bg): Mp 169–171 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1658; ^1H NMR (60 MHz, DMSO- d_6) δ =1.32 and 1.51 (s, s, 3H), 2.21 (s, 3H), 2.30 (s, 3H), 2.57–3.02 (m, 3H), 7.01–8.20 (m, 13H), and 9.81 (br. s, 1H). Found: C, 68.72; H, 5.80; N, 3.18%. Calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}_4$: C, 69.10; H, 5.80; N, 3.10%.

6,6-Bis(4-methylphenyl)-4-carbamoyl-3-methyl-1,2-dioxan-3-ol (3bh): Mp 194–197 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1641; ^1H NMR (60 MHz, DMSO- d_6) δ =1.18 and 1.42 (s, s, 3H), 2.22 (s, 3H), 2.27 (s, 3H), 2.78–3.02 (m, 3H), 6.67 and 6.83 (s, s, 1H), 6.92 (br. s, 2H), and 6.93–7.59 (m, 8H). Found: C, 70.38; H, 6.77; N, 4.11%. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_4$: C, 70.38; H, 6.79; N, 4.10%.

6,6-Bis(4-fluorophenyl)-4-(phenylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3cb): Mp 185–188 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1646; ^1H NMR (60 MHz, DMSO- d_6) δ =1.23 and 1.52 (s, s, 3H), 2.61–3.11 (m, 3H), 6.85 and 7.03 (s, s, 1H), 7.04–7.92 (m, 13H), and 9.81 (br. s, 1H). Found: C, 67.80; H, 4.95; N, 3.31%. Calcd for $\text{C}_{24}\text{H}_{21}\text{F}_2\text{NO}_4$: C, 67.75; H, 4.98; N, 3.30%.

6,6-Bis(4-fluorophenyl)-4-(dimethylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3cj): Mp 162–164 °C (from benzene–hexane); IR (KBr) ν 3380 and 1627; ^1H NMR (60 MHz, DMSO- d_6) δ =1.08 and 1.38 (s, s, 3H), 2.89 (s, 3H), 2.97 (s, 3H), 2.68–3.11 (m, 3H), 6.80 and 6.98 (s, s, 1H), and 6.92–7.86 (m, 8H). Found: C, 63.84; H, 5.65; N, 3.66%. Calcd for $\text{C}_{20}\text{H}_{21}\text{F}_2\text{NO}_4$: C, 63.65; H, 5.61; N, 3.71%.

6,6-Bis(4-chlorophenyl)-4-(2-chlorophenylcarbamoyl)-1,2-dioxan-3-ol (3dg): Mp 154–156 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1658; ^1H NMR (60 MHz, DMSO- d_6) δ =1.35 and 1.51 (s, s, 3H), 2.62–3.01 (m, 3H), 7.13 and 7.25 (s, s, 1H), 7.15–8.12 (m, 12H), and 9.81 (br. s, 1H). Found: C, 57.97; H, 4.17; N, 2.91%. Calcd for $\text{C}_{24}\text{H}_{20}\text{Cl}_3\text{NO}_4$: C, 58.49; H, 4.10; N, 2.84%.

6,6-Bis(4-chlorophenyl)-4-(dimethylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3dj): Mp 191–192 °C (from benzene–hexane); IR (KBr) ν 3292 and 1617; ^1H NMR (60 MHz, DMSO- d_6) δ =1.18 and 1.42 (s, s, 3H), 2.58 (s, 3H), 2.65 (s, 3H), 2.66–3.13 (m, 3H), 6.75 and 6.98 (s, s, 1H), and 7.32–7.61 (m, 8H). Found: C, 58.57; H, 5.20; N, 3.37%. Calcd for $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{NO}_4$: C, 58.54; H, 5.16; N, 3.31%.

4-(2-Chlorophenylcarbamoyl)-6,6-bis(4-methoxyphenyl)-3-methyl-1,2-dioxan-3-ol (3eg): Mp 124–126 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1655; ^1H NMR (60 MHz, DMSO- d_6) δ =1.30 and 1.52 (s, s, 3H), 2.66–3.04 (m, 3H), 3.71 (s, 3H), 3.77 (s, 3H), 6.83–8.33 (m, 13H), and 9.81 (br. s, 1H). Found: C, 64.48; H, 5.47; N, 3.08%. Calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}_6$: C, 64.53; H, 5.42; N, 2.91%.

6,6-Bis(4-methoxyphenyl)-4-(dimethylcarbamoyl)-3-methyl-1,2-dioxan-3-ol (3ej): Mp 200–201 °C (from benzene–hexane); IR (KBr) ν 3192 and 1608; ^1H NMR (60 MHz, DMSO- d_6) δ =1.08 and 1.34 (s, s, 3H), 2.88 (s, 3H), 2.96 (s, 3H), 2.64–3.13 (m, 3H), 3.71 (s, 3H), 3.77 (s, 3H), 6.73 and 7.01 (s, s, 1H), and 6.83–7.63 (m, 8H). Found: C, 65.67; H, 6.78; N, 3.48%. Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_6$: C, 65.82; H, 6.78; N, 3.79%.

4-(Phenylcarbamoyl)-6,6-diethyl-3-methyl-1,2-dioxan-3-ol (3fb): Mp 149–152 °C (from benzene–hexane); IR (KBr) ν 3500–3100 and 1642; ^1H NMR (60 MHz, DMSO- d_6) δ =0.72–1.13 (m, 6H), 1.28–2.31 (m, 7H), 2.72–3.08 (m, 3H), 6.50 and 6.83 (s, s, 1H), 7.01–8.02 (m, 5H), and 9.77 (br. s, 1H); ^{13}C NMR (DMSO- d_6) δ =169.789, 169.595, 138.999, 138.701, 128.632, 128.587, 123.411, 123.142, 119.443, 119.147,

101.706, 97.499, 81.970, 80.672, 47.526, 46.064, 32.130, 29.609, 27.953, 27.867, 24.015, 22.777, 24.478, 19.868, 7.502, 7.397, 7.342, and 6.965. Found: C, 65.63; H, 7.62; N, 5.01%. Calcd for C₁₆H₂₃NO₄: C, 65.51; H, 7.90; N, 4.78%.

4-(4-Chlorophenylcarbamoyl)-6,6-diethyl-3-methyl-1,2-dioxan-3-ol (3ff): Mp 157–159 °C (from benzene-hexane); IR (KBr) ν 3500–3100 and 1658; ¹H NMR (60 MHz, DMSO-*d*₆) δ =0.63–1.08 (m, 6H), 1.28–2.31 (m, 7H), 2.66–3.12 (m, 3H), 6.50 and 6.83 (s, s, 1H), 7.22–7.78 (m, 4H), and 9.93 (br. s, 1H); ¹³C NMR (DMSO-*d*₆) δ =169.799, 169.596, 137.927, 137.673, 128.484, 128.371, 126.962, 126.724, 120.981, 101.618, 97.456, 81.961, 80.659, 47.526, 46.214, 32.037, 29.417, 27.825, 27.821, 24.017, 22.764, 24.465, 19.885, 7.489, 7.384, 7.381, and 6.966. Found: C, 58.49; H, 6.62; N, 4.35%. Calcd for C₁₆H₂₂ClNO₄: C, 58.62; H, 6.73; N, 4.27%.

3-(4-Methylphenylcarbamoyl)-2-methyl-5,5-diphenyl-4,5-dihydrofuran (4aa): Mp 251–252 °C (from ethanol); IR (KBr) ν 3264 and 1657; ¹H NMR (60 MHz, DMSO-*d*₆) δ =2.23 (s, 3H), 2.30 (t, *J*=1.2 Hz, 3H), 3.73 (q, *J*=1.2 Hz, 2H), 6.98–7.68 (m, 14H), and 9.81 (br. s, 1H). Found: C, 81.34; H, 6.33; N, 3.72%. Calcd for C₂₅H₂₃NO₂: C, 81.26; H, 6.28; N, 3.79%.

Methylation of 4-(Phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ab). Anhydrous potassium carbonate (180 mg) and dimethyl sulfate (170 mg) were added to compound **3ab** (389 mg) in anhydrous acetone (5 cm³). The mixture was heated under reflux for 10 h. Water (5 cm³) was added to the mixture after cooling and the acetone was removed. The residue was extracted with chloroform (total 60 cm³) and the extract was dried over anhydrous magnesium sulfate. After the removal of the chloroform, the crude product was chromatographed on a silica-gel column while eluting with benzene to give *c*-4-(phenylcarbamoyl)-*r*-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane (**5ab**) (197 mg, 49% yield), and *t*-4-(phenylcarbamoyl)-*r*-3-methoxy-6,6-diphenyl-1,2-dioxane (**5ab'**) (141 mg, 35% yield).

c-4-(Phenylcarbamoyl)-r-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane (5ab): Mp 186–187 °C (from benzene-hexane); IR (KBr) ν 3308 and 1664; ¹H NMR (400 MHz, CDCl₃) δ =1.299 (s, 3H), 2.826–2.856 (m, *J*=13.20, 14.83, and 4.57 Hz, 2H), 2.970 (dd, *J*=14.83 and 4.57 Hz, 1H), 3.449 (s, 3H), 7.110–7.605 (m, 15H), and 8.807 (s, 1H); ¹³C NMR (CDCl₃) δ =169.316, 143.405, 140.481, 137.840, 128.979, 128.592, 128.323, 127.786, 127.592, 126.995, 125.921, 124.266, 119.820, 100.860, 85.704, 50.439, 49.350, 33.806, and 18.918. Found: C, 74.39; H, 6.33; N, 3.45%. Calcd for C₂₅H₂₅NO₄: C, 74.42; H, 6.25; N, 3.47%.

t-4-(Phenylcarbamoyl)-r-3-methoxy-3-methyl-6,6-diphenyl-1,2-dioxane (5ab'): Mp 176–177 °C (from benzene-hexane); IR (KBr) ν 3340 and 1692; ¹H NMR (400 MHz, CDCl₃) δ =1.336 (s, 3H), 2.531 (t, *J*=13.92 Hz, 1H), 3.032–3.076 (d, *J*=13.92 Hz, 2H), 3.489 (s, 3H), 7.11–7.49 (m, 15H), and 7.78 (s, 1H); ¹³C NMR (CDCl₃) δ =168.463, 145.684, 141.507, 137.703, 129.066, 128.514, 128.320, 127.738, 126.187, 125.799, 124.292, 119.593, 106.556, 87.208, 50.018, 48.243, 32.863, and 14.545. Found: C, 74.39; H, 6.31; N, 3.49%. Calcd for C₂₅H₂₅NO₄: C, 74.42; H, 6.25; N, 3.47%.

Acetylation of 4-(Phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3ab). Compound **3ab** (389 mg) was treated with a mixture of acetic anhydride (102 mg), pyridine (14 mg), and triethylamine (121 mg) at room temperature overnight. The reaction mixture was concentrated to dryness in vacuo and the residue was dissolved in benzene (30 cm³). The

benzene solution was washed with 2 M (1 M=1 moldm⁻³) hydrochloric acid (30 cm³), and with a saturated aqueous sodium hydrogencarbonate solution, then dried over anhydrous magnesium sulfate. After the removal of the benzene, the residue was chromatographed on a silica-gel column while eluting with benzene, giving *c*-4-(phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-*r*-3-ol acetate (**6ab**) (232 mg, 54% yield), and *t*-4-(phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-*r*-3-ol acetate (**6ab'**) (91 mg, 21% yield).

c-4-(Phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-r-3-ol Acetate (6ab): Mp 186–187 °C (from benzene-hexane); IR (KBr) ν 3320, 1731, and 1665; ¹H NMR (60 MHz, CDCl₃) δ =1.70 (s, 3H), 2.15 (s, 3H), 2.76–3.36 (m, 3H), 7.06–7.68 (m, 15H), and 7.83 (s, 1H); ¹³C NMR (CDCl₃) δ =167.538, 167.448, 142.760, 140.299, 137.360, 129.170, 128.708, 128.484, 128.230, 127.664, 126.768, 125.724, 124.859, 119.966, 103.259, 85.790, 50.555, 32.833, 22.212, and 21.332. Found: C, 72.50; H, 5.85; N, 3.28%. Calcd for C₂₆H₂₅NO₅: C, 72.37; H, 5.84; N, 3.25%.

t-4-(Phenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-r-3-ol Acetate (6ab'): Mp 153–154 °C (from benzene-hexane); IR (KBr) ν 3382, 1732, and 1690; ¹H NMR (60 MHz, CDCl₃) δ =1.73 (s, 3H), 2.21 (s, 3H), 2.78–3.23 (m, 3H), 7.13–7.66 (m, 15H), and 7.83 (s, 1H); ¹³C NMR (CDCl₃) δ =168.836, 167.657, 145.341, 141.051, 137.434, 129.111, 128.588, 128.365, 127.977, 127.335, 126.052, 125.575, 124.680, 119.802, 109.047, 86.939, 48.362, 32.953, 22.257, and 17.424. Found: C, 72.45; H, 5.84; N, 3.24%; Calcd for C₂₆H₂₅NO₅: C, 72.37; H, 5.84; N, 3.25%.

Catalytic Hydrogenation of 4-(4-Methylphenylcarbamoyl)-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3aa). (a) In acetic acid. A mixture of **3aa** (403 mg) and 5% palladium on charcoal (20 mg) in ethyl acetate (5 cm³) was stirred under an atmosphere of hydrogen at room temperature for 3 h. The reaction mixture was filtered and the filtrate was concentrated to dryness. The solidified residue was recrystallized from benzene, giving 3-(4-methylphenylcarbamoyl)-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**4aa**) (86% yield): Mp 251–252 °C; (b) In ethanol. Hydrogenation of **3aa** similar to (a) but in ethanol yielded 3-(4-methylphenylcarbamoyl)-2-methyl-5,5-diphenyltetrahydro-2-furanol (**7aa**) (80% yield): Mp 225–227 °C (from ethanol); IR (KBr) ν 3600–3100, and 1642; ¹H NMR (60 MHz, DMSO-*d*₆) δ =1.57 (s, 3H), 2.22 (s, 3H), 2.81–3.12 (m, 3H), 6.11 (s, 1H), 7.03–7.67 (m, 14H), and 9.66 (br. s, 1H). Found: C, 77.51; H, 6.50; N, 3.60%. Calcd for C₂₅H₂₅NO₃: C, 77.49; H, 6.50; N, 3.61%.

Dehydration of 7aa. Compound **7aa** (194 mg) was dissolved in acetic acid (0.5 cm³) and the solution was heated under reflux for 1 h. After the removal of the acetic acid, the residue was recrystallized from benzene, giving **4aa** (87% yield): Mp 251–252 °C, identical with that obtained from the preceding experiment (a).

Decomposition of 3aa with Methanolic Potassium Hydroxide. A mixture of **3aa** (202 mg) and 5% KOH-MeOH (10 cm³) was heated under reflux for 2 h. After the removal of the methanol, Water (20 cm³) was added, and the mixture was extracted with benzene (total 60 cm³). The benzene solution was washed with dilute hydrochloric acid (30 cm³), a saturated aqueous sodium hydrogencarbonate solution (20 cm³), and water (20 cm³), and then dried over anhydrous magnesium sulfate. After the removal of the benzene, the resulting mixture was chromatographed on a silica-gel plate while eluting with benzene, yielding benzophenone (66 mg, 72% yield).

Reaction of Xanthene with *N*-Phenylacetoacetamide (2b) in the Presence of Manganese(III) Acetate. [Mn(OAc)₃] (536 mg) was added to a solution of xanthene (180 mg) and **2b** (707 mg) in acetic acid (30 cm³) at 100 °C. The reaction mixture was heated at the same temperature until the dark-brown color of the solution turned opaque white (approximately 3 min). After the removal of the solvent under reduced pressure, the residue was treated with 2 M hydrochloric acid (30 cm³) and extracted with chloroform (25 cm³×3). The products were separated on a silica-gel column, while eluting with chloroform, and recrystallized.

***N*-Phenyl-2-(9-xanthenyl)acetoacetamide (8).** (182.1 mg, 51% yield): Mp 203–204 °C (from ethanol); IR (KBr) ν 3328, 1719, and 1659; ¹H NMR (60 MHz, DMSO-*d*₆) δ =1.99 (s, 3H), 3.90 (d, *J*=10.0 Hz, 1H), 3.87 (d, *J*=10.0 Hz, 1H), 6.8–7.6 (m, 13H), and 9.91 (br. s, 1H). Found: C, 77.09; H, 5.31; N, 4.09%. Calcd for C₂₃H₁₉O₃N: C, 77.29; H, 5.36; N, 3.92%. Xanthene (34.5 mg, 19% yield) and *N*-phenylacetoacetamide (**2a**, 69.2 mg, 10% yield) were recovered.

Reaction of 1,1-Diphenylethene (1a) with Manganese(III) Acetate. A mixture of **1a** (180 mg) and [Mn(OAc)₃] (268 mg) in acetic acid (30 cm³) was stirred at 23 °C under an air stream for 12 h. The reaction mixture was worked-up in a manner similar to that described above, giving 2,2-diphenyl-2-hydroxyethyl acetate (**9**) (10.2 mg, 4% yield, mp 87–88 °C (lit.¹⁰ mp 91 °C)), benzophenone (12.7 mg, 7% yield), and unreacted **1a** (147.6 mg, 82% yield).

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