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Reaction of Olefins with Malonamide in the Presence of Manganese(III) Acetate. Formation of α,β-Unsaturated γ-Lactones and γ-Lactams

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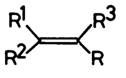
The reaction of olefins with malonamide in the presence of manganese(III) acetate gave 2-buten-4-olides and/or 1*H*-pyrrol-2(5*H*)-ones in one-step, short reaction time, and moderate yields. The product distribution can be accounted for in terms of the stabilization of the intermediate carbocation in the oxidation process. The synthetic application and limitation, and the oxidation mechanism for the formations of α,β-unsaturated γ-lactones and γ-lactams are discussed.

It is known that ketones have been oxidized with manganese(III) acetate, $Mn(OAc)_3$, in acetic acid to form α-keto radicals, $\cdot CH_2COR$.[1,2] If the reaction is carried out in the presence of olefins, the α-keto radicals add to the olefins to give radical adducts which are converted to saturated or unsaturated ketones, or γ-keto esters either by gaining or losing hydrogen, or by further oxidation and taking up an acetate ion.[3] On the other hand, oxidation of readily enolizable ketones, such as β-diketones, with $Mn(OAc)_3$ gives the corresponding α,α′-diketo radicals, $RCO\dot{C}H$-COR.[4] Heiba and Dessau reported that acetylacetone was oxidized with $Mn(OAc)_3$ in the presence of olefins to form dihydrofurans in high yields.[5] In contrast, it was reported that the reaction of olefins and malonic acid in a 2:1 molar ratio (equivalent) in the presence of $Mn(OAc)_3$ yielded spirodi-γ-lactones in high yields.[6]

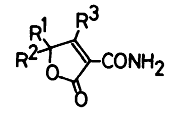
Recently, the author attempted the intramolecular oxidative cyclization of aromatic secondary amines with $Mn(OAc)_3$.[7] However, *N*-cyclized products were not obtained. These results led me to investigate the reaction of olefins with malonamide in the presence of $Mn(OAc)_3$. As the result, it was found that 2-buten-4-olides and/or 1*H*-pyrrol-2(5*H*)-ones were produced, but the desired spirodi-γ-lactams were not formed. In this paper, I will discuss the synthetic application and limitation, and the oxidation mechanism for the formations of α,β-unsatutrated γ-lactones and γ-lactams.

Results and Discussion

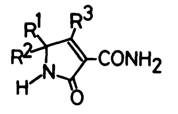
When malonamide was oxidized with $Mn(OAc)_3$ in the presence of 1,1-diphenylethene (**1a**), the reaction was finished within 1 min to give **2a**, **4a**, and benzophenone (**5a**). The major product **2a** showed a characteristic vinylic proton (δ=8.71) of 2-buten-4-olides in the lower field[8] and two broad singlets assigned to an amino group of which one was hydrogen-bonded according to the ^1H-NMR spectrum. Its IR spectrum revealed two carbonyl absorption bands and one olefinic absorption band. Therefore, the structure of **2a** was considered to be 2-carbamoyl-4,4-diphenyl-2-buten-4-olide, which was compatible with its mass spectrum. The minor product **4a** was determined to be 3,3,8,8-tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,



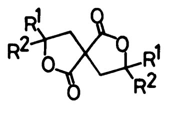
1a–j : R=H
8g,h,j : R=OAc
11 : $R^1=R^2=R^3=$4-MeOPh, R=CHO



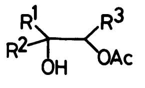
2a-h



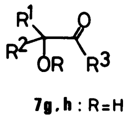
3f-j
3f′: R^3=OH



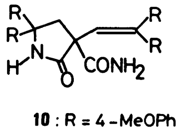
4a,b,k



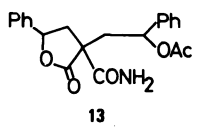
6a,c,g–i



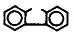
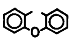
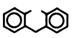
7g,h : R=H
7j : R=Ac



10 : R = 4-MeOPh



13

a : $R^1=R^2=$Ph, R^3=H
b : R^1=Me, R^2=Ph, R^3=H
c : $R^1=R^2=R^3$=Ph
d : R^1, R^2= , R^3=COOH
e : R^1, R^2=$\leftarrow CH_2 \rightarrow_5$, R^3=H
f : $R^1=R^2=$4-MeOPh, R^3=H
g : $R^1=R^2=$4-MeOPh, R^3=Ph
h : $R^1=R^2=R^3$=4-MeOPh
i : R^1, R^2= , R^3=Ph
j : R^1, R^2= , R^3=Ph
k : R^1=Ph, $R^2=R^3$=H

6-dione of which ^{1}H-NMR, IR spectra, and the melting point were identical with those of an authentic sample.[6] The same reaction of 2-phenylpropene (**1b**), 1,1,2-triphenylethene (**1c**), fluorenylideneacetic acid (**1d**), and methylenecyclohexane (**1e**) gave the corresponding 2-buten-4-olides in moderate yields (Table 1).

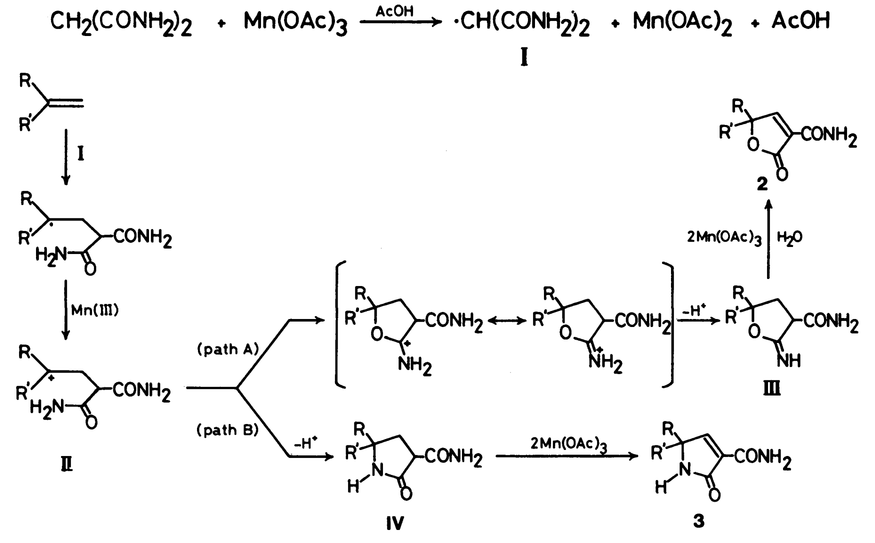
On the other hand, when 1,1-bis(4-methoxyphenyl)-ethene (**1f**) was oxidized under the same reaction conditions, α,β-unsaturated γ-lactams (**3f** and **3f′**) were produced rather than the corresponding 2-buten-4-olide (**2f**). The structure of **3f** was determined to be 3-carbamoyl-5,5-bis(4-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one on the basis of the ^{1}H-NMR, ^{13}C-NMR, IR, and mass spectra. The ^{1}H-NMR spectrum of **3f′** was similar to that of **3f** except for the disappearance of a doublet assignable to a H-4 proton and the appearance of a broad singlet (δ=5.38) due to a hydroxyl group. Accordingly, the compound **3f′** was confirmed to be 3-carbamoyl-4-hydroxy-5,5-bis(4-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one. 3-Carbamoyl-3-[2,2-bis(4-methoxyphenyl)ethenyl]-5,5-bis(4-methoxyphenyl)-2-pyrrolidone (**10**) was also obtained.

The formation of the α,β-unsaturated γ-lactams deserves comment. It seems that the intermediate carbocation (**II**) tends to cyclize with a nitrogen atom of the carbamoyl group when it is stabilized by the resonance effect of the methoxyl group (Scheme 1). Then, the reaction of 1,1-bis(4-methoxyphenyl)-2-phenylethene (**1g**), 1,1,2-tris(4-methoxyphenyl)ethene (**1h**), 9-benzylidene-9*H*-xanthene (**1i**), and 9-benzylidene-9,10-dihydroanthracene (**1j**) with malonamide in the presence of Mn(OAc)$_3$ was tried. The reaction of **1g** or **1h** under the same reaction conditions certainly gave the corresponding α,β-unsaturated γ-lactam (**3g** or **3h**). However, the olefins (**1g** and **1h**) were also oxidized directly by Mn(OAc)$_3$ without the participation of malonamide to yield products (**5g**, **6g** and **6h**, **7g** and **7h**, **8g** and **8h**, and **9g** and **9h**). The same oxidation of **1i** and **1j** afforded the corresponding 1*H*-pyrrol-2-(5*H*)-ones (**3i** and **3j**) in good yields, as expected.

Table 1. Reaction of olefins with malonamide in the presence of manganese(III) acetate

	Molar ratio[a)]	Time	Recovery	Product (yield/%)[b)]								
		min	%									
1a	1 : 4 : 3	1	13	**2a**(56)		**4a**(5)	**5a**(4)					
1b	1 : 6 : 4	1		**2b**(38)		**4b**(3)	**5b**(4)					
1c	1 : 8 : 6	3	2	**2c**(69)				**6c**(8)				
1d	1 : 4 : 4	0.1		**2d**(48)			**5d**(5)					
1e	1 : 6 : 6	1		**2e**(26)								
1f	1 : 6 : 4	1	1	**2f**(9)	**3f**(18)	**3f′**(20)						**10**(11)
1g	1 : 10 : 4	2		**2g**(14)	**3g**(17)		**5g**(9)	**6g**(27)	**7g**(18)	**8g**(19)	**9g**(20)	
1h	1 : 10 : 4	2		**2h**(4)	**3h**(5)		**5g**(20)	**6h**(18)	**7h**(16)	**8h**(8)	**9h**(11)	**11**(3)
1i	1 : 10 : 4	1			**3i**(59)		**5i**(29)	**6i**(17)				**12**(20)
1j	1 : 10 : 4	0.2			**3j**(90)				**7j**(2)	**8j**(5)		

a) Substrate : malonamide : manganese(III) acetate. b) The yields were based on the amount of the substrate used.



Scheme 1.

It is suggested that this reaction consists of two competing mechanisms. One is the direct oxidation of the substrate with $Mn(OAc)_3$ without the participation of malonamide (product **5**, **6**, **7**, **8**, and **9**). This mechanism has been explained as the electron-transfer mechanism represented by the aromatic acetoxylation[9] or the oxidation of α-glycols[10] with $Mn(OAc)_3$ alone. The other is a radical mechanism involving the malonamide radical (**I**) (product **2**, **3**, **4**, **10**, and **13**). The mechanism for the formation of the α,β-unsaturated γ-lactones and γ-lactams as depicted in Scheme 1 is deduced from the reaction of olefins with acetylacetone in the presence of $Mn(OAc)_3$.[5] At first, malonamide is readily oxidized with $Mn(OAc)_3$ to give the corresponding radical (**I**) which attacks olefins to form a benzyl radical. Then, the benzyl radical is subsequently oxidized to generate the intermediate carbocation (**II**). If cyclization occurs at the carbonyl oxygen of the carbamoyl group of the carbocation **II**, the imine **III** is formed (path A). The intermediate **III** is further oxidized and hydrolyzed upon work-up to give the α,β-unsaturated γ-lactone (**2**). When the carbocation **II** cyclizes on a nitrogen atom of the carbamoyl group, the pyrrolidone **IV** is elaborated and further oxidized to yield the *1H*-pyrrol-2(*5H*)-one **3** (path B). It seems that it depends on the lifetime of **II** whether the carbocation **II** cyclizes on oxygen or nitrogen atom of the carbamoyl group. That is to say, when the carbocation **II** is stabilized by the delocalization of a positive charge, the carbocation **II** cyclizes on a nitrogen atom of the carbamoyl group. In fact, **1f**—**h** having two or three methoxyl groups or **1i**, **j** having a large molecular structure which can delocalize the positive charge produced the corresponding 1*H*-pyrrol-2(5*H*)-ones. 4-Butanolides derived from an attack on the olefins of the carboxymethyl radical (which was generated directly by the thermolysis of $Mn(OAc)_3$[11]) were not detected. This indicates that the malonamide radical (**I**) rather than the carboxymethyl radical was preferentially produced by the reaction. The malonamide radical (**I**) might be generated by the direct interaction of malonamide and $Mn(OAc)_3$, which is similar to the aromatic acetonylation mechanism reported by Kurz *et al.*[12] In view of the product yield, it seems that the radical mechanism prefers the electron-transfer mechanism under these reaction conditions (except for **1g** and **1h**).

This reaction of styrene (**1k**) gave not only α,β-unsaturated γ-lactone and γ-lactam, but also spirodi-γ-lactones (**4k**) and γ-lactone (**13**). Cyclohexene, cyclooctene, octene, and acenaphthylene under the same reaction conditions resulted in an intractable mixture. Therefore, it is thought that the formation of α,β-unsaturated γ-lactones and γ-lactams using this reaction is effective for the polar olefins, such as the 1,1-disubstituted olefins. Although it is well known that olefins are oxidized with $Mn(OAc)_3$ in acetic acid to afford γ-lactones in good yields,[11] this reaction is the first example that α,β-unsaturated γ-lactones and/or γ-lactams are produced in one-step, with a short reaction time, and in moderate yields.

Experimental

Measurements. All melting points are uncorrected. The ^{1}H-NMR spectra were recorded on a Hitachi Perkin-Elmer R-24 (60 MHz) or a JEOL JNM-GX-270 spectrometer (270 MHz) at room temperature. The ^{13}C-NMR spectra were obtained with a JEOL JNM-GX-270 spectrometer (68 MHz). All chemical shifts are recorded in the δ scale relative to TMS as an internal standard. The IR spectra were taken on a JASCO A-102 infrared spectrophotometer and all IR spectral data are expressed in cm^{-1}. The mass spectra were measured on a JEOL JMS-DX-300 mass spectrometer using a direct-insertion probe at 70 eV ionizing voltage.

Materials. The olefins (**1a**—**c**, **e**—**g**) and manganese(III) acetate dihydrate used were prepared according to a method described in the literature.[6,14] Fluorenylideneacetic acid (**1d**) was obtained by the standard procedure[15] from fluorenone and ethyl bromoacetate, mp 231.7—232.7 °C (lit,[16] mp 232 °C). 9-Benzylidene-9*H*-xanthene (**1i**) and 9-benzylidene-9,10-dihydroanthracene (**1j**) were synthesized from 9-xanthenone and anthrone, **1i**: mp 114—115 °C (EtOH) (lit,[17] mp 116 °C); Anal. ($C_{20}H_{14}O$) C, H, and **1j**: mp 133.0—133.5 °C (benzene); Anal. ($C_{21}H_6$) C, H. Styrene, cyclooctene, octene, acenaphthylene, and malonamide were obtained from a commercial sample of the Wako Pure Chemical Industries, Ltd.

Reaction of Olefins with Malonamide. The typical procedure for the reaction of olefins with malonamide in the presence of manganese(III) acetate was as follows. To a heated solution of olefin (1 or 2 mmol) and malonamide in acetic acid (25 ml), manganese(III) acetate was added (see Table 1). The solution was heated under reflux until the brown color of Mn(III) ion disappeared. The solvent was removed *in vacuo* and the residue was triturated with 2 M hydrochloric acid ($1 M=1 mol dm^{-3}$), followed by extraction with chloroform. The products were separated on TLC (Wakogel B-10) with chloroform or diethyl ether as the developing solvent. The yields are summarized in Table 1.

*Oxidation Products of 1,1-Diphenylethene (**1a**).* *2-Carbamoyl-4,4-diphenyl-2-buten-4-olide (**2a**)*: Colorless needles (from benzene/light petroleum), mp 167.5—168.0 °C; IR ($CHCl_3$) 3500—3200 (NH_2), 1757 and 1685 (C=O), and 1645 (C=C); ^{1}H-NMR ($CDCl_3$) δ=6.30 (1H, br. s, NH), 7.30 (10H, s, ArH), 7.67 (1H, br. s, NH), and 8.71 (1H, s, H-3); MS *m/z* 279 (M^+), 262, 236, 202, 189, 174, 165, 131, and 105. Found: *m/z* 279.08925. Calcd for $C_{17}H_{13}O_3N$: M, 279.08954.

*3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**4a**)*: Colorless needles (from benzene), mp 285 °C (lit,[6] mp 284.5—285.0 °C).

*Benzopenone (**5a**)*: Colorless plates (from methanol), mp 47—48 °C (lit,[18] mp 47—48 °C).

*Oxidation Products of 2-Phenylpropene (**1b**).* *2-Carbamoyl-4-methyl-4-phenyl-2-buten-4-olide (**2b**)*: Colorless plates (from benzene/light petroleum), mp 151—153 °C; IR ($CHCl_3$) 3500—3200 (NH_2), 1755 and 1684 (C=O), and

1643 (C=C); ^{1}H-NMR (CDCl$_3$) δ=1.87 (3H, s, CH$_3$), 6.41 (1H, br. s, NH), 7.37 (5H, s, ArH), 7.75 (1H, br. s, NH), and 8.46 (1H, s, H-3); MS m/z (rel intensity), 217 (M$^+$, 12), 202 (40), 175 (100), 158 (66), 131 (74), 105 (100), and 77 (70). Found: C, 66.20; H, 5.29; N, 6.33%. Calcd for $C_{12}H_{11}O_3N$: C, 66.35; H, 5.10; N, 6.45%.

3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (4b): It was confirmed by the ^{1}H-NMR spectrum that this compound consisted of three stereoisomers, (3*R**, 5*R**, 8*R**), (3*S**, 5*R**, 8*S**), and (3*R**, 5*R**, 8*S**).[6]

Acetophenone (5b): The product **5b** was identical with an authentic sample.

Oxidation Products of 1,1,2-Triphenylethene (1c). 2-Carbamoyl-3,4,4-triphenyl-2-buten-4-olide (2c): Colorless needles (from benzene), mp 230—231 °C; IR (CHCl$_3$) 3500—3100 (NH$_2$), 1744 and 1688 (C=O), and 1629 (C=C); ^{1}H-NMR (CDCl$_3$) δ=6.03 (1H, br. s, NH), 6.7—7.5 (15H, m, ArH), and 7.94 (1H, br. s, NH); MS m/z (rel intensity), 355 (M$^+$, 16), 338 (12), 309 (18), 292 (11), 266 (19), 182 (12), 165 (13), 145 (100), 129 (87), 105 (80), and 77 (57). Found: m/z 355.11970. Calcd for $C_{23}H_{17}O_3N$: M, 355.12084.

1,1,2-Triphenyl-1,2-ethanediol 2-Acetate (6c): Colorless microcrystals (from benzene), mp 227 °C (lit,[6] mp 224.5—225.5 °C).

Oxidation Products of Fluorenylideneacetic Acid (1d). 4′-Carbamoylspiro[fluorene-9,2′(5′H)-furan]-5′-one (2d): Pale yellow needles (from benzene/light petroleum), mp 241.5—242.5 °C; IR (CHCl$_3$) 3600—3100 (NH$_2$), 1758 and 1687 (C=O), and 1640 (C=C); ^{1}H-NMR (DMSO-d_6) δ=6.95—7.93 (10H, m, ArH and NH$_2$), 8.12 (1H, s, H-4); MS m/z (rel intensity), 277 (M$^+$, 100), 260 (95), 232 (81), 222 (88), 205 (66), 189 (62), 176 (63), and 165 (52). Found: m/z 277.07332. Calcd for $C_{17}H_{11}O_3N$: M, 277.07389.

9-Fluorenone (5d): All spectral data of **5d** were compatible with an authentic sample.

Oxidation Product of Methylenecyclohexane (1e). 3-Carbamoyl-1-oxaspiro[4.5]dec-3-en-2-one (2e): Colorless needles (from benzene/light petroleum), mp 154—155 °C; IR (CHCl$_3$) 3500—3200 (NH$_2$), 1741 and 1684 (C=O), and 1642 (C=C); ^{1}H-NMR (CDCl$_3$) δ=1.74 (10H, br. s, 5×-CH$_2$-), 6.90 (1H, br. s, NH), 7.78 (1H, br. s, NH), and 8.32 (1H, s, H-4); MS m/z (rel intensity), 195 (M$^+$, 4), 178 (100), and 152 (13). Found: C, 61.81; H, 6.79; N, 7.02%. Calcd for $C_{10}H_{13}O_3N$: C, 61.52; H, 6.71; N, 7.18%.

Oxidation Products of 1,1-Bis(4-methoxyphenyl)ethene (1f). 2-Carbamoyl-4,4-bis(4-methoxyphenl)-2-buten-4-olide (2f): Colorless prisms (from benzene/light petroleum), mp 157 °C; IR (CHCl$_3$) 3500—3200 (NH$_2$), 1752 and 1683 (C=O), and 1643 (C=C); ^{1}H-NMR (CDCl$_3$) δ=3.75 (6H, s, 2×OCH$_3$), 6.35 (1H, br. s, NH), 6.74—7.26 (8H, m, ArH), 7.68 (1H, br. s, NH), and 8.64 (1H, s, H-3); MS m/z (rel intensity), 339 (M$^+$, 37), 322 (3), 295 (100), 251 (22), 237 (13), 204 (58), 161 (21), 135 (100), and 107 (20). Found: m/z 339.10658. Calcd for $C_{19}H_{17}O_5N$: M, 339.11067.

*3-Carbamoyl-5,5-bis(4-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one (3f)*: Colorless needles (from chloroform/light petroleum), mp 203 °C; IR (CHCl$_3$) 3500—3100 (NH$_2$), 1700 and 1671 (C=O), and 1631 (C=C); ^{1}H-NMR (DMSO-d_6) δ=3.74 (6H, s, 2×OCH$_3$), 6.83—7.36 (8H, m, ArH), 7.68 (1H, br. s, NH), 7.98 (1H, br. s, NH), 8.48 (1H, d, J=1.8 Hz, H-4), and 10.00 (1H, br. d, J=1.8 Hz, NH); ^{13}C-NMR (CD$_3$OD) δ=55.8, 70.6, 115.1, 128.5, 129.3, 133.2, 142.6, 160.9, 164.8, and 171.6; MS m/z (rel intensity), 338 (M$^+$, 2), 321 (7), 294 (100), 280 (46), 231 (9), 158 (10), 134 (49), and 119 (12). Found: m/z 338.12978. Calcd for $C_{19}H_{18}O_4N_2$: M, 338.12666.

*3-Carbamoyl-4-hydroxy-5,5-bis(4-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one (3f′)*: Colorless needles (from chloroform/light petroleum), mp 130—131 °C; IR (CHCl$_3$) 3500—3100 (NH and OH), 1653 (C=O), and 1618 (C=C); ^{1}H-NMR (CDCl$_3$) δ=3.79 (6H, s, 2×OCH$_3$), 5.38 (1H, br. s, OH), 6.45 (1H, br. s, NH), 6.84—7.32 (8H, m, ArH), 7.59 (1H, br. s, NH), and 8.32 (1H, br. s, NH); ^{13}C-NMR (CD$_3$OD) δ=55.8 (q), 88.0 (s), 95.4 (s), 114.8 (d), 129.4 (d), 131.4 (s), 161.4 (s), 168.2 (s), 179.2 (s), and 194.4 (s); MS m/z (rel intensity), 354 (M$^+$, 35), 311 (82), 294 (25), 226 (100), 211 (100), 195 (16), 183 (18), 168 (17), 152 (19), 135 (43), 113 (52), 92 (11), and 77 (19). Found: m/z 354.12294. Calcd for $C_{19}H_{18}O_5N_2$: M, 354.12157.

3-Carbamoyl-3-[2,2-bis(4-methoxyphenyl)ethenyl]-5,5-bis(4-methoxyphenyl)-2-pyrrolidone (10): Colorless microcrystals (from carbon tetrachloride/light petroleum), mp 121—124 °C; IR (CHCl$_3$) 3550—3100 (NH), 1692 (C=O), and 1606 (C=C); ^{1}H-NMR (CDCl$_3$) δ=2.57 (1H, d, J=13.2 Hz, CH$_2$), 3.31 (1H, d, J=13.2 Hz, CH$_2$), 3.67 (3H, s, OCH$_3$), 3.72 (3H, s, OCH$_3$), 3.75 (3H, s, OCH$_3$), 3.78 (3H, s, OCH$_3$), 5.87 (1H, br. s, NH), 6.12 (1H, s, =CH-), 6.57—7.26 (17H, m, ArH and NH), and 8.25 (1H, s, NH); MS m/z (rel intensity), 578 (M$^+$, 3), 535 (100), 492 (15), 427 (11), 384 (8), 371 (30), 295 (39), 265 (20), 227 (74), 189 (19), 134 (19), and 121 (38). Found: m/z 578.24302. Calcd for $C_{35}H_{34}O_6N_2$: M, 578.24169.

Oxidation Products of 1,1-Bis(4-methoxyphenyl)-2-phenylethene (1g). 2-Carbamoyl-4,4-bis(4-methoxyphenyl)-3-phenyl-2-buten-4-olide (2g): Colorless microcrystals (from benzene/light petroleum), mp 98—99 °C; IR (CHCl$_3$) 3600—3100 (NH$_2$), 1741 and 1684 (C=O); ^{1}H-NMR (CDCl$_3$) δ=3.71 (6H, s, 2×OCH$_3$), 6.15 (1H, br. s, NH), 6.57—7.40 (13H, m, ArH), and 7.80 (1H, br. s, NH); MS m/z (rel intensity), 415 (M$^+$, 40), 371 (60), 329 (25), 242 (30), 227 (20), and 135 (100). Found: m/z 415.14532. Calcd for $C_{25}H_{21}O_5N$: M, 415.14197.

*3-Carbamoyl-5,5-bis(4-methoxyphenyl)-4-phenyl-1*H*-pyrrol-2(5*H*)-one (3g)*: Colorless needles (from chloroform/light petroleum), mp 134—136, 225—226 °C; IR (CHCl$_3$) 3600—3100 (NH), and 1698 (C=O); ^{1}H-NMR (DMSO-d_6) δ=3.74 (6H, s, 2×OCH$_3$), 6.65—7.35 (13H, m, ArH), 7.38 (1H, br. s, NH), 8.01 (1H, br. s, NH), and 9.48 (1H, s, NH); MS m/z (rel intensity), 414 (M$^+$, 45), 371 (100), 307 (50), 240 (40), 210 (45), 134 (55), and 77 (12). Found: m/z 414.15650. Calcd for $C_{25}H_{22}O_4N_2$: M, 414.15796.

4,4′-Dimethoxybenzophenone (5g): Colorless plates (from ethanol), mp 143—144 °C (lit,[19] mp 144 °C).

1,1-Bis(4-methoxypheny)-2-phenyl-1,2-ethanediol 2-Acetate (6g): Colorless microcrystals (from benzene), mp 200—201 °C; IR (CHCl$_3$) 3600—3100 (OH) and 1735 (OAc); ^{1}H-NMR (CDCl$_3$) δ=1.96 (3H, s, OAc), 2.67 (1H, s, OH), 3.70 (3H, s, OCH$_3$), 3.80 (3H, s, OCH$_3$), 6.54 (1H, s, >CH-), and 6.67—7.51 (13H, m, ArH). Found: C, 73.55; H, 6.10%. Calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16%.

2-Hydroxy-2,2-bis(4-methoxyphenyl)-1-phenylethanone (7g): Colorless needles (from benzene/light petroleum), mp 138—140 °C; IR (CHCl$_3$) 3600—3100 (OH) and 1666 (C=O); ^{1}H-NMR (CDCl$_3$) δ=3.63 (6H, s, 2×OCH$_3$), 4.93 (1H, br. s, OH), 6.60—7.80 (13H, m, ArH); MS m/z (rel intensity), 348 (M$^+$, 5), 242 (100), 227 (65), 211 (85), 135 (70), and 107 (70). Found: m/z 348.13133. Calcd for $C_{22}H_{20}O_4$: M, 348.13616.

1-Acetoxy-2,2-bis(4-methoxyphenyl)-1-phenylethene (8g):

Colorless microcrystals (from ethanol), mp 101—102 °C; IR ($CHCl_3$) 1753 (OAc); ^{1}H-NMR ($CDCl_3$) δ=1.95 (3H, s, OAc), 3.67 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 6.55—7.45 (13H, m, ArH); MS *m/z* (rel intensity), 374 (M^+, 10), 332 (28), 278 (14), 242 (30), 223 (30), 212 (52), 205 (12), 196 (92), 180 (41), 168 (25), 149 (100), 135 (70), and 107 (10). Found: *m/z* 374.15023. Calcd for $C_{24}H_{22}O_4$: M, 374.15181.

*Benzoic Acid (**9g**)*: ^{1}H-NMR and IR spectral data were in agreement with an authentic sample.

*Oxidation Products of 1,1,2-Tris(4-methoxyphenyl)ethene (**1h**).* *2-Carbamoyl-3,4,4-tris(4-methoxyphenyl)-2-buten-4-olide (**2h**)*: Colorless microcrystals (from benzene/light petroleum), mp 118—119 °C; IR ($CHCl_3$) 3600—3100 (NH_2), 1736 and 1680 (C=O); ^{1}H-NMR ($CDCl_3$) δ=3.76 (9H, s, 3× OCH_3), 5.8 (1H, br. s, NH), 6.60—7.22 (12H, m, ArH), and 8.0 (1H, br. s, NH). Found: *m/z* 445.15133. Calcd for $C_{26}H_{23}O_6N$: M, 445.15254.

*3-Carbamoyl-4,5,5-tris(4-methoxyphenyl)-1*H*-pyrrol-2(5*H*)-one (**3h**)*: Colorless needles (from chloroform/light petroleum), mp 188—189 °C; IR ($CHCl_3$) 3600—3100 (NH) and 1692 (C=O); ^{1}H-NMR (DMSO-d_6) δ=3.70 (3H, s, OCH_3), 3.72 (6H, s, 2×OCH_3), 6.65—7.30 (12H, m, ArH), 7.38 (1H, br. s, NH), 8.01 (1H, br. s, NH), and 9.46 (1H, s, NH). Found: *m/z* 444.17383. Calcd for $C_{26}H_{24}O_5N_2$: M, 444.16852.

*1,1,2-Tris(4-methoxyphenyl)-1,2-ethanediol 2-Acetate (**6h**)*: Colorless microcrystals (from benzene), mp 187.0—187.5 °C; IR ($CHCl_3$) 3600—3200 (OH) and 1734 (OAc); ^{1}H-NMR ($CDCl_3$) δ=1.95 (3H, s, OAc), 2.79 (1H, s, OH), 3.73 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.83 (3H, s, OCH_3), 6.61—7.61 (12H, m, ArH), and 6.83 (1H, s, >CH-). Found: C, 70.91; H, 6.32%. Calcd for $C_{25}H_{26}O_6$: C, 71.07; H, 6.20%.

*2-Hydroxy-1,2,2-tris(4-methoxyphenyl)-1-ethanone (**7h**)*: Colorless needles (from benzene/light petroleum), mp 118—119 °C; IR ($CHCl_3$) 3600—3200 (OH) and 1654 (C=O); ^{1}H-NMR ($CDCl_3$) δ=3.72 (9H, s, 3×OCH_3), 5.20 (1H, br. s, OH), and 6.68—7.82 (12H, m, ArH). Found: *m/z* 378.14591. Calcd for $C_{23}H_{22}O_5$: M, 378.14673.

*1-Acetoxy-1,2,2-tris(4-methoxyphenyl)ethene (**8h**)*: Liquid; IR ($CHCl_3$) 1751 (OAc); ^{1}H-NMR ($CDCl_3$) δ=1.98 (3H, s, OAc), 3.71 (6H, s, 2×OCH_3), 3.78 (3H, s, OCH_3), and 6.60—7.25 (12H, m, ArH); MS *m/z* (rel intensity), 404 (M^+, 25), 362 (50), 333 (23), 242 (48), 194 (40), and 152 (100). Found: *m/z* 404.16293. Calcd for $C_{25}H_{24}O_5$: M, 404.16238.

p-*Anisic Acid (**9h**)*: ^{1}H-NMR and IR spectral data were compatible with an authenitic sample.

*2,3,3-Tris(4-methoxyphenyl)-2-propenal (**11**)*: Colorless needles (from light petroleum), mp 126—127 °C; IR ($CHCl_3$) 1723 (CHO); ^{1}H-NMR ($CDCl_3$) δ=3.78 (9H, s, 3×OCH_3), 6.73—7.30 (12H, m, ArH), and 10.13 (1H, s, CHO); MS *m/z* (rel intensity), 374 (M^+, 3), 333 (100), 242 (78), 227 (80), 211 (70), 135 (70), and 107 (47). Found: *m/z* 374.15161. Calcd for $C_{24}H_{22}O_4$: M, 374.15181.

*Oxidation Products of 9-Benzylidene-9*H*-xanthene (**1i**).* *4-Carbamoyl-3-phenyl-1,5-dihydrospiro[2*H*-pyrrole-2,9'-xanthen]-5-one (**3i**)*: Colorless prisms (from ethanol), mp 251 °C; IR (KBr) 3600—3000 (NH) and 1697 (C=O); ^{1}H-NMR (DMSO-d_6) δ=6.50—7.48 (13H, m, ArH), 7.52 (1H, br. s, NH), 8.20 (1H, br. s, NH), and 9.80 (1H, s, NH); MS *m/z* (rel intensity), 368 (M^+, 100), 351 (16), 325 (81), 295 (7), 281 (12), 222 (30), 204 (20), 195 (40), 168 (12), 146 (28), and 129 (60). Found: *m/z* 368.11536. Calcd for $C_{23}H_{16}O_3N_2$: M, 368.11609.

*9-Xanthenone (**5i**)*: Colorless needles (from ethanol), mp 175 °C (lit,[20] mp 173—174 °C). Found: C, 79.38; H, 4.16%. Calcd for $C_{13}H_8O_2$: C, 79.58; H, 4.11%.

*9-(α-Acetoxybenzyl)-9-xanthenol (**6i**)*: Colorless microcrystals (from benzene), mp 141—142 ° C; IR ($CHCl_3$) 3600—3100 (OH) and 1740 (OAc); ^{1}H-NMR ($CDCl_3$) δ=1.93 (3H, s, OAc), 3.90 (1H, br. s, OH), 5.87 (1H, s, >CH-), and 6.38—7.70 (13H, m, ArH). Found: *m/z* 346.12230. Calcd for $C_{22}H_{18}O_4$: M, 346.12051.

*α,α-Diacetoxytoluene (**12**)*: Colorless microcrystals (from light petroleum), mp 45 °C (lit,[21] mp 45—46 °C); IR ($CHCl_3$) 1758 (OAc); ^{1}H-NMR ($CDCl_3$) δ=2.01 (6H, s, 2×OAc), 7.23—7.52 (5H, m, ArH), and 7.55 (1H, s, >CH-).

*Oxidation Products of 9-Benzylidene-9,10-dihydroanthracene (**1j**).* *4'-Carbamoyl-3'-phenyl-1',5'-dihydrospiro[anthracene-9(10*H*), 2'-[2*H*]pyrrol]-5'-one (**3j**)*: Colorless microcrystals (from ethanol), mp 248—249 °C; IR (KBr) 3600—3100 (NH) and 1670 (C=O); ^{1}H-NMR (DMSO-d_6) δ=2.94 (2H, br. s, CH_2), 5.71 (1H, br. s, NH), and 6.8—7.9 (15H, m, ArH and NH_2); MS *m/z* (rel intensity), 366 (M^+, 43), 293 (100), 233 (54), 208 (46), and 91 (29). Found: *m/z* 366.13415. Calcd for $C_{24}H_{18}O_2N_2$: M, 366.13683.

*9-Acetoxy-9-benzoyl-9,10-dihydroanthracene (**7j**)*: Colorless needles (from light petroleum), mp 151.5—152.0 °C; IR ($CHCl_3$) 1751 (OAc) and 1663 (C=O); ^{1}H-NMR ($CDCl_3$) δ= 2.12 (3H, s, OAc), 3.31 (2H, s, CH_2), and 6.0—8.2 (13H, m, ArH). Found: *m/z* 342.12724. Calcd for $C_{23}H_{18}O_3$: M, 342.12560.

*9-(α-Acetoxybenzylidene)-9,10-dihydroanthracene (**8j**)*: Pale yellow needles (from ethanol), mp 214 °C; IR ($CHCl_3$) 1762 (OAc) and 1622 (C=C); ^{1}H-NMR ($CDCl_3$) δ=2.59 (3H, s, OAc), 4.94 (2H, s, CH_2), and 7.0—8.3 (13H, m, ArH). Found: *m/z* 326.12870. Calcd for $C_{23}H_{18}O_2$: M, 326.13068.

*Reaction of Styrene (**1k**) with Malonamide in the Presence of Manganese(III) Acetate.* The reaction was carried out by the same procedure described above (molar ratio, **1k**: malonamide:$Mn(OAc)_3$=1:4:4; reaction time, 1 min).

*3,8-Diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**4k**)*: Three stereoisomers (yield; 4%) were isolated; (3*R**, 5*R**, 8*R**), mp 162—163 °C (lit,[6] mp 162—163 °C); (3*S**, 5*R**, 8*R**), mp 185—186 °C (lit, [6] mp 185—186 °C); (3*S**, 5*R**, 8*S**), mp 239—240 °C (lit,[6] mp 236—237 °C).

*2-(2-Acetoxy-2-phenylethyl)-2-carbamoyl-4-phenyl-4-butanolide (**13**)*: Yield, 5%; colorless needles (from benzene/ light petroleum), mp 184—185 °C; IR ($CHCl_3$) 3600—3100 (NH_2), 1752 and 1687 (C=O); ^{1}H-NMR ($CDCl_3$) δ= 2.07 (3H, s, OAc), 2.54 (2H, m, H-3), 2.93 (2H, d, *J*=8.4 Hz, CH_2), 5.42 (1H, t, *J*=8.4 Hz, >CH-), 5.81 (1H, br. s, NH), 5.93 (1H, dd, *J*=10.8 and 3.0 Hz, H-4), 7.15 (1H, br. s, NH), and 7.27 (5H, s, ArH); MS *m/z* (rel intensity), 367 (M^+, 1), 324 (2), 307 (2), 264 (6), 247 (25), 205 (100), 188 (65), 170 (67), 162 (58), 144 (11), 129 (37), 116 (25), 105 (68), and 77 (46). Found: *m/z* 367.13929. Calcd for $C_{21}H_{21}O_5N$: M, 367.14197.

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