Reaction of Olefins with α-Cyanoacetamide in the Presence of Manganese(III) Acetate

Hidehiko SATO, Hiroshi NISHINO,* and Kazu KUROSAWA
Department of Chemistry, Faculty of Science, Kumamoto University,
Kurokami 2-39-1, Kumamoto 860
(Received October 3, 1986)

2-Butenamides and 2-buten-4-olides are formed by the reaction of phenyl or 4-chlorophenyl-substituted olefins with α-cyanoacetamide in the presence of manganese(III) acetate. On the other hand, aryl substituted olefins having electron-donating groups are oxidized under similar reaction conditions to give 1,5-dihydro-2*H*-pyrrol-2-ones and 3-ethenyl-2-pyrrolidones. All these reactions also produce glycols or ketones which are given by the direct oxidation of these olefins with manganese(III) acetate. The question whether an intermediate carbocation in the oxidation process cyclized on an oxygen or a nitrogen atom can be explained by the hard and soft acids and bases (HSAB) concept. A possible mechanism for the formation of 2-butenamides and 2-buten-4-olides is proposed.

Recently, some useful annulation reactions using manganese(III) salts have been reported. Manganese(III) acetate oxidation of alkenes in acetic acid gave γ-lactones,[1] and similar oxidation in the presence of malonic acid or substituted acetic acid yielded spirodi-γ-lactones[2] or α-substituted γ-lactones.[3] On the other hand, alkenes were oxidized with tris(2,4-pentanedionato)manganese(III) to produce dihydrofurans in good yields.[4] One of the authors tried spirodilactamization by the manganese(III) oxidation of malonamide in the presence of alkenes. However, this oxidation did not give spiroannulated products, but α,β-unsaturated γ-lactones and γ-lactams along with other products.[5] This prompted us to investigate the synthesis of γ-lactam analogs, which might be bioactive new compounds or precursors of naturally occurring compounds, by the use of α-cyanoacetamide instead of malonamide. It was found that the reaction gave γ-lactams and γ-lactones together with some other products. We will describe these results and discuss the factors which may govern the mode of the cyclization either on a nitrogen atom or an oxygen atom in the acetamide group.

Results and Discussion

When a mixture of 1,1-diphenylethene (**1a**) and α-cyanoacetamide was oxidized with manganese(III) acetate, products **2a** and **3a** were obtained together with small amounts of **4a**, **5a**, **8a**, **9a**, and benzophenone (**10a**) (Table 1, Entry 1). The ^{1}H NMR spectrum of **2a** showed a singlet due to a vinylic proton at δ 8.51 and the ^{13}C NMR spectrum exhibited three singlets assigned to two carbonyl carbons and a cyano carbon. The IR spectrum of **2a** revealed a characteristic absorption band due to α,β-unsaturated nitrile. These spectral data indicated that the structure of **2a** was 4-acetoxy-2-cyano-4,4-diphenyl-2-butenamide. However, the configuration of the C=C double bond in **2a** could not be determined. The structures of **3a**, **4a**, **5a**, **8a**, and **9a** were determined to be 2-cyano-4,4-diphenyl-2-buten-4-olide, 2-carbamoyl-4,4-diphenyl-2-buten-4-olide, 2-cyano-2-(2,2-diphenylethenyl)-4,4-diphenyl-4-butanolide, 3-cyano-3-(2,2-diphenylethenyl)-5,5-diphenyl-2-pyrrolidone, and 4-acetoxy-2-cyano-4,4-diphenylbutanamide, respectively, on the basis of their spectral data. When a similar reaction was carried out under anhydrous conditions, the carbamoylbutenolide (**4a**) was not formed (Entry

Table 1. Reaction of 1,1-Diphenylethene (**1a**) with α-Cyanoacetamide in the Presence of Manganese(III) Acetate at the Reflux Temperature

Entry	Molar ratio[a]	Time / min	Recovery / %	Product (yield/%)[b]						
				2a	**3a**	**4a**	**5a**	**8a**	**9a**	**10a**
1	1 : 1 : 4	1	3	22	15	2	3	5	3	2
2	1 : 2 : 4	1	5	21	14	2	4	8	5	2
3[c]	1 : 2 : 4	1	3	25	13		4	6	5	3
4	1 : 4 : 4	1	6	20	13	3	4	10	4	2
5	1 : 1 : 6	66		7	13	20	9	10		8
6	1 : 2 : 6	20		14	14	9	7	9		5
7	1 : 6 : 6	1	1	12	12	5		8	2	3

a) **1a** : $CH_2(CN)CONH_2$: manganese(III) acetate. b) The yields are based on the amount of the **1a** used. c) Acetic anhydride (10 equivalents) was added.

3). On the other hand, the oxidation in a molar ratio of **1a**:α-cyanoacetamide:manganese(III) acetate=1:1:6 gave **4a** as the main product and the yield of **2a** decreased, although the reaction time has become longer (Entry 5). It suggests that the **2a** could be hydrolyzed under the reaction conditions to yield **4a**. In fact, the **2a** gave **4a** (27%) on treatment with six molar equivalents of manganese(II) acetate tetrahydrate, $[Mn(OAc)_2]\cdot 4H_2O$, in boiling acetic acid for 2 h. The cyanobutenolide (**3a**) was also hydrolyzed in the presence of manganese(II) acetate tetrahydrates to yield **4a** (21%). However, this route (**3a**→**4a**) would not be important because the **3a** was constantly produced irrespective of the molar ratio.

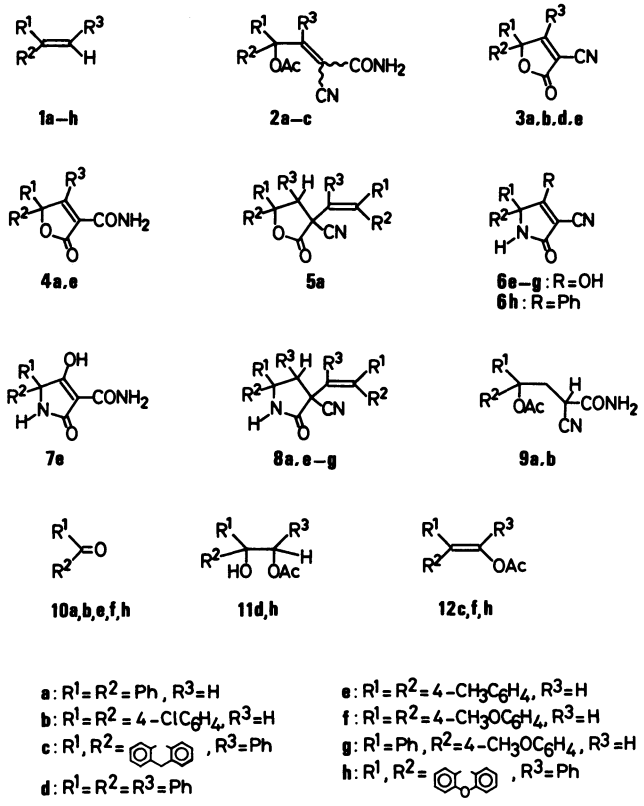


Fig. 1.

The similar oxidations of 1,1-bis(4-chlorophenyl)-ethene (**1b**), 9-benzylidene-9,10-dihydroanthracene (**1c**), and 1,1,2-triphenylethene (**1d**) mainly produced butenamides (**2b** an **2c**) and butenolides (**3b** and **3d**) (Table 2, Entries 2-4).

On the other hand, 1,1-bis(4-methoxyphenyl)ethene (**1f**) was oxidized under similar reaction conditions to yield 3-cyano-4-hydroxy-5,5-bis(4-methoxyphenyl)-1,5-dihydro-2*H*-pyrrol-2-one (**6f**) and 3-cyano-3-[2,2-bis(4-methoxyphenyl)ethenyl]-5,5-bis(4-methoxyphenyl)-2-pyrrolidone (**8f**) along with small amounts of 4,4′-dimethoxybenzophenone (**10f**) and 1-acetoxy-2,2-bis(4-methoxyphenyl)ethene (**12f**) (Table 2, Entry 6).

It has already been discussed that the reaction of aryl-substituted olefins having electron-donating groups with malonamide tends to give such *N*-cyclized products as 1,5-dihydro-2*H*-pyrrol-2-ones.[5] Reactions of 1-(4-methoxyphenyl)-1-phenylethene (**1g**) and 9-benzylidene-9*H*-xanthene (**1h**) with α-cyanoacetamide also yielded 1,5-dihydro-2*H*-pyrrol-2-ones (**6g** and **6h**) and 3-ethenyl-2-pyrrolidone (**8g**). However, the oxidation of **1h** mainly gave 9-xanthenone (**10h**), 9-(α-acetoxybenzyl)-9-xanthenol (**11h**), 9-(α-acetoxybenzylidene)-9*H*-xanthene (**12h**), and α,α-diacetoxytoluene (**14**), which would be formed via an electron-transfer mechanism. This mechanism is well-known in manganese(III) acetate oxidation.[1d,6]

The structure of manganese(III) acetate has been erroneously described in organic chemistry to be a simple acetate, $[Mn(OAc)_3]\cdot 2H_2O$, until a recent date.[5,7,8] However, Fristad et al. explained the radical mechanism for the manganese(III)-mediated γ-lactone annulation by use of the correct structure of manganese(III) acetate: oxygen-centered triangle, $[Mn_3O(OAc)_6(OAc)(HOAc)]\cdot 5H_2O$.[1c,9] In the manganese(III)-α-cyanoacetamide system, a similar mechanism can be considered (Scheme 1), and compound **3** or **6** would be formed via path A. On path A, it was assumed that butanolide(**I**) might be a precursor of **3** and **5**. When 2-cyano-4,4-diphenyl-4-butanolide

Table 2. Reaction of Olefins (**1a**—**h**) with α-Cyanoacetamide in the Presence of Manganese(III) Acetate at the Reflux Temperature[a,b]

Entry	Substrate	Recovery(%)	Product (yield/%)[c]						
1	**1a**	5	**2a** (21)	**3a** (14)	**4a** (2)	**5a** (4)	**8a** (8)	**9a** (5)	**10a** (2)
2	**1b**	11	**2b** (24)	**3b** (15)	**9b** (7)	**10b** (6)			
3	**1c**	5	**2c** (30)	**12c** (30)	**13** (22)				
4	**1d**	39	**3d** (30)	**10a** (trace)		**11d** (5)			
5	**1e**		**3e** (5)	**4e** (7)	**6e** (3)	**7e** (1)	**8e** (44)	**10e** (3)	
6	**1f**		**6f** (23)	**8f** (33)	**10f** (5)	**12f** (3)			
7	**1g**		**6g** (7)	**8g** (37)					
8	**1h**	1	**6h** (14)	**10h** (26)	**11h** (40)	**12h** (7)	**14** (27)		

a) **1** : $CH_2(CN)CONH_2$: manganese(III) acetate = 1 : 2 : 4. b) The reactions were terminated within 1 min. c) The yields are based on the amount of the substrate used.

(**I**, $R^1=R^2=Ph$), which was prepared by an alternative method,[3c,3d,10] was oxidized with manganese(III) acetate, **3a** was not formed, while the oxidation of **I** ($R^1=R^2=Ph$) in the presence of **1a** gave rise to **5a**. Therefore, one can consider another pathway (path B) for the formation of **3** or **6** via 2-cyano-3-butenamide (**III**) as a reaction intermediate. The intermediate **III** was not isolated from the reaction products, probably because **III** was more liable to be oxidized than the parent olefin under the reaction conditions. However, the involvement of **III** is suggested by the fact that 2,2-diphenylethenylmalonate (**15**) was actually isolated together with 2-ethoxycarbonyl-4,4-diphenyl-2-buten-4-olide (**16**) in the manganese(III)-mediated reaction of **1a** with diethyl malonate and that the **15** was subsequently converted to **16** under the reaction conditions (Table 3).

The cyclization of carbocation (**II** or **IV**) depends on whether **II** or **IV** is "hard" or "soft" on the basis of the hard and soft acids and bases (HSAB) concept.[12] That is to say, when the cation is relatively hard (as in the cases of **1a—d**), it cyclizes on an oxygen atom to give butenolide (**3**), while the reaction of **1f—h** yields 1,5-dihydro-2*H*-pyrrol-2-one (**6**) since the carbocation derived from **1f—h** is relatively soft. This tendency is also the case for the reaction with malonamide.[5] Both *O*-cyclized (**3e** and **4e**) and *N*-cyclized products (**6—8e**) were obtained by the reaction of **1e**, indicating that the corresponding carbocation (**IV**) has an intermediate

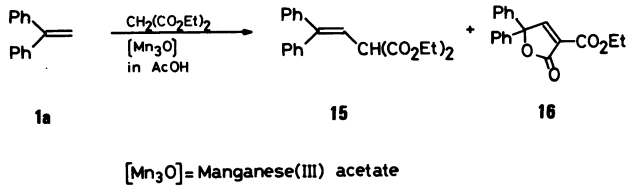
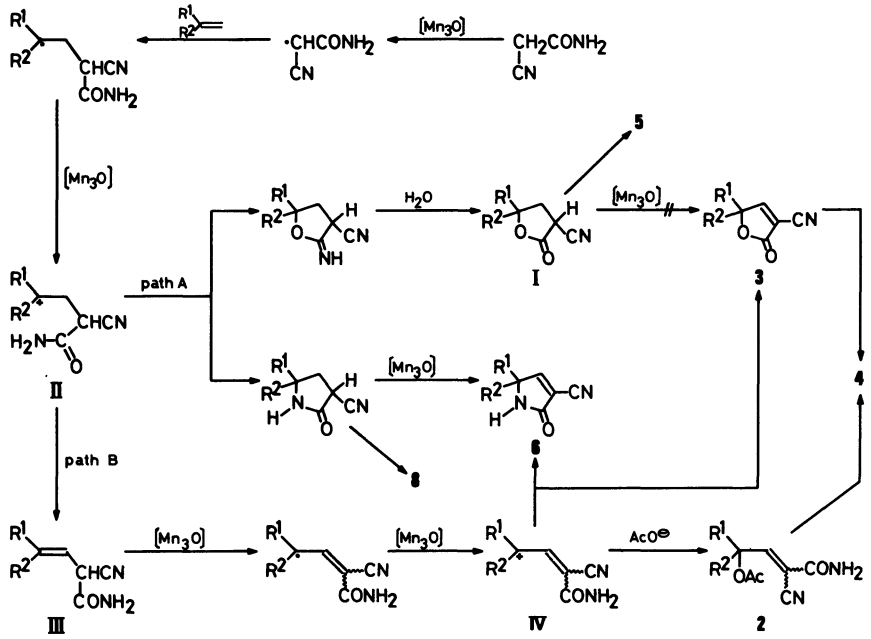


Fig. 2.



Scheme 1.

Table 3. Reaction of 1,1-Diphenylethene (**1a**) with Diethyl Malonate in the Presence of Manganese(III) Acetate and Oxidation of the Product (**15**)[a]

Entry	Substrate	Molar ratio[b]	Time / min	Recovery / %	Product (yield/%)[c]	
					15	**16**
1	**1a**	1 : 1 : 3	3	28	26	20
2	**1a**	1 : 1 : 4	5	12	26	40
3	**1a**	1 : 1 : 5	6		22	56
4	**1a**	1 : 1 : 6	90			70
5	**15**	1 : 2[d]	5	29		48
6	**15**	1 : 4[d]	210			75

a) The reactions were carried out at the reflux temperature. b) Substrate : $CH_2(CO_2Et)_2$: manganese(III) acetate. c) The yields are based on the amount of the substrate used. d) **15** : manganese(III) acetate.

nature of "hard and soft acids." It seems that the formation of **2** depends on the configuration of **IV**. When the configuration of the cyano group and the $-\overset{+}{C}R^1R^2$ group on **IV** is cis, the **IV** could not cyclize on a nitrogen atom of nitrile, but was probably attacked by an acetate ion to give **2**.

In conclusion, the reaction of olefins with α-cyanoacetamide gave 2-butenamides, 2-buten-4-olides, 1,5-dihydro-2*H*-pyrrol-2-ones, and 3-ethenyl-2-pyrrolidones; these are more complex than the products in the reaction with malonamide.[5] Although the cyano group on α-cyanoacetamide is favorable to the formation of the $\cdot CH(CN)CONH_2$ radical, the cyano group itself is not so reactive in these reactions: the cyclization involving the cyano group did not occur. The reason for the absence of spiroannulation products in the reaction with α-cyanoacetamide or diethyl malonate could be ascribed to the preferential formation of **III** via path B and to the difficulty of the spiroannulation of **5** and **8** involving the cyano group. Moreover, the formation of **3** and **6** could be explained by the HSAB concept.

Experimental

Measurements. Melting points were determined with an Electrothermal apparatus and are uncorrected. The IR spectra were taken on a JASCO A-102 infrared spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Hitachi Perkin-Elmer R-24 (60 MHz) and a JEOL FX-100 instrument at room temperature. The mass spectra were obtained with a JEOL JMS-DX-300 mass spectrometer using a direct-insertion probe at an ionizing voltage of 70 eV.

Materials. The olefin (**1a—h**) and manganese(III) acetate used were prepared according to methods described in the literature.[5] α-Cyanoacetamide, diethyl malonate, and manganese(II) acetate tetrahydrate were obtained from commercial samples from the Wako Pure Chemical Industries, Ltd.

Reaction of Olefins with α-Cyanoacetamide. The typical procedure for the reaction of olefins with α-cyanoacetamide in the presence of manganese(III) acetate was as follows. To a heated solution of olefin (1 mmol) and α-cyanoacetamide (2 mmol) in acetic acid (25 cm^3), manganese(III) acetate (4 mmol) which was calculated based on the formula weight of $[Mn(OAc)_3 \cdot 2H_2O]$[5] was added. The mixture was heated under reflux until the color of Mn(III) ion changed from brown to transparent. The solvent was removed in vacuo and the residue was triturated with 2 M (1 M=1 mol dm^{-3}) hydrochloric acid (25 cm^3), followed by extraction with chloroform. The products were separated on TLC (Wakogel B-10 or Kieselgel 60G) with chloroform or diethyl ether as the developing solvent. The characteristic data of the new compounds are summarized in Table 4. All spectral data and the melting points of known compounds were identical with those reported in the literatures.

Oxidation Products. 1a: 2a, 3a, 4a,[5] **5a, 8a, 9a,** and **10a.**[5] **1b**: 4-Acetoxy-4,4-bis(4-chlorophenyl)-2-cyano-2-butenamide (**2b**), 4,4-bis(4-chlorophenyl)-2-cyano-2-buten-4-olide (**3b**), 4-acetoxy-4,4-bis(4-chlorophenyl)-2-cyanobutanamide (**9b**), and 4,4'-dichlorobenzophenone (**10b**).[11]

1c: 3-(9-Acetoxy-9,10-dihydro-9-anthryl)-2-cyano-3-phenylpropenamide (**2c**), 9-(α-acetoxybenzylidene)-9,10-dihydroanthracene (**12c**),[5] and 9-acetoxy-9-benzoyl-9,10-dihydroanthracene (**13**).[5]

1d: 2-Cyano-3,4,4-triphenyl-2-buten-4-olide (**3d**), **10a**, 2-acetoxy-1,1,2-triphenylethanol (**11d**).[5]

1e: 2-Cyano-4,4-bis(4-methylphenyl)-2-buten-4-olide (**3e**), 2-carbamoyl-4,4-bis(4-methylphenyl)-2-buten-4-olide (**4e**), 3-cyano-4-hydroxy-5,5-bis(4-methylphenyl)-1,5-dihydro-2*H*-pyrrol-2-one (**6e**), 3-carbamoyl-4-hydroxy-5,5-bis(4-methylphenyl)-1,5-dihydro-2*H*-pyrrol-2-one (**7e**), 3-cyano-3-[2,2-bis(4-methylphenyl)ethenyl]-5,5-bis(4-methylphenyl)-2-pyrrolidone (**8e**), and 4,4'-dimethylbenzophenone (**10e**).[12]

1f: **6f, 8f, 10f,**[13] and **12f.**[14]

1g: 3-Cyano-4-hydroxy-5-(4-methoxyphenyl)-5-phenyl-1,5-dihydro-2*H*-pyrrol-2-one (**6g**) and 3-cyano-3-[2-(4-methoxyphenyl)-2-phenylethenyl]-5-(4-methoxyphenyl)-5-phenyl-2-pyrrolidone (**8g**). The stereochemistry of **6g** and **8g** was not determined.

1h: 4-Cyano-3-phenyl-1,5-dihydrospiro[2*H*-pyrrole-2,9'-xanthen]-5-one (**6h**), **10h,**[15] **11h,**[5] **12h,**[4] and **14.**[16]

Hydrolyses of 2a and 3a. When **2a** (174.0 mg) was treated with manganese(II) acetate tetrahydrate (803.5 mg) in acetic acid (25 cm^3) for 2 h at reflux temperature, **4a** (41.8 mg, 27%) and **2a** (52.0 mg, 30% recovered) were obtained. On the other hand, **3a** (168.9 mg) and manganese(II) acetate tetrahydrate (636.9 mg) were heated under reflux in acetic acid (25 cm^3) for 80 min, giving **4a** (38.0 mg, 21%) and **3a** (90.4 mg, 53% recovered).

Synthesis of 2-Cyano-4,4-diphenyl-4-butanolide (I). A mixture of **1a** (903.5 mg), cyanoacetic acid (3.401 g), and manganese(III) acetate (2.746 g) was heated in acetic acid (50 cm^3) at 70 °C for 15 min according to Fristad method.[3b] On cooling, water (200 cm^3) was added to it and the aqueous solution was extracted with ether. The ethereal extract was washed with aqueous sodium hydrogencarbonate solution and then water. The reaction products were purified on TLC, giving colorless liquid **I** (650.2 mg, 49%). All spectral data were identical with those of the literature.[3b]

Oxidation of 2-Cyano-4,4-diphenyl-4-butanolide (I) with Manganese(III) Acetate. The butanolide **I** (183.6 mg) was oxidized with manganese(III) acetate (373.9 mg) in acetic acid (25 cm^3). The mixture was heated under reflux for 3 min and gave a tarry material, but the butenolide (**3a**) was not detected.

The Reactions of 1,1-Diphenylethene (1a) and 2-Cyano-4,4-diphenyl-4-butanolide (I). A mixture of **1a** (154.5 mg), **I** (223.0 mg), and manganese(III) acetate (457.2 mg) was heated under reflux in acetic acid (25 cm^3) for 1 min. After treatment by the procedure described above, a mixture of **5a** and 3-cyano-1,1,5,5-tetraphenyl-4-penten-1-ol (115.7 mg, 31% yield as **5a**) was obtained and **1a** was recovered (29%).

3-Cyano-1,1,5,5-tetraphenyl-4-penten-1-ol: Colorless prisms (from light petroleum), mp 105.0—105.5 °C; IR ($CHCl_3$) 2236 (CN) and 3200—3600 (OH); ^1H NMR ($CDCl_3$) δ=2.28 (1H, s, OH), 2.6—2.9 (2H, m, CH_2), 3.2—3.7 (1H, m, >CH–), 5.92 (1H, d, J=9.6 Hz, =CH–), and 6.7—7.6 (20H, m, 4×Ph). Found: C, 86.44; H, 6.00; N, 3.32%. Calcd for $C_{30}H_{25}ON$: C, 86.71; H, 6.06; N, 3.37%.

Reaction of 1,1-Diphenylethene (1a) with Diethyl Malonate in the Presence of Manganese(III) Acetate. To a heated solution of **1a** (1 mmol), diethyl malonate (1 mmol), and

Table 4. Characteristic Data of the New Compounds

Compd	Mp θ_m/°C	IR[a] cm^{-1}	^{1}H and ^{13}C NMR[b] δ	MS *m/z* (rel int)	Analysis	
					Formula	Found(Calcd)
2a	169.7—170.3 (benzene)	1226(C-O-C) 1623(C=C) 1701(C=O) 1748(C=O) 2220(CN) 3100—3600(NH_2)	2.21(3H, s, OAc), 6.17(2H, br. s, NH_2), 7.1—7.5(10H, m, 2×Ph), 8.51(1H, s, =CH-); 21.1(q, CH_3), 84.0(s, C-O), 106.0 (s, =C<), 115.0(s, CN), 127.0(d, Arom. C), 128.5(d, Arom. C), 128.6(d, Arom. C), 140.6(s, Arom. C), 158.0(d, =CH-), 161.0(s, $CONH_2$), 168.7(s, O-CO-)	320(M^+, 5) 278(12) 261(32) 217(75) 173(100) 105(70) 77(40) 43(100)	$C_{19}H_{16}O_3N_2$	*m/z* 320.1142 (M, 320.1161)
2b	187.6—188.1 (CCl_4)	1216(C-O-C) 1623(C=C) 1702(C=O) 1753(C=O) 2220(CN) 3100—3600(NH_2)	2.21(3H, s, OAc), 6.31(2H, br. s, NH_2), 7.23(8H, s, Arom. H), 8.38(1H, s, =CH-)		$C_{19}H_{14}O_3N_2Cl_2$	C 58.56(58.63) H 3.60(3.63) N 7.16(7.20)
2c	112.8—113.7 (benzene/hexane)	1225(C-O-C) 1683(C=O) 1744(C=O) 2200(CN) 3100—3500(NH_2)	2.11(3H, s, OAc), 3.42(2H, s, CH_2), 4.9(1H, br. s, NH_2), 6.02 (1H, br. s, NH_2), 6.3—6.8(2H, m, Arom. H), 6.8—7.7(10H, m, Arom. H), 7.9—8.2(1H, m, Arom. H)	408(M^+, 17) 348(26) 275(100) 232(16)	$C_{26}H_{20}O_3N_2$	*m/z* 408.1477 (M, 408.1474)
3a	140.5—141.5 (methanol)	1627(C=C) 1786(C=O) 2240(CN)	7.1—7.6(10H, m, 2×Ph), 8.50(1H, s, =CH-)	261(M^+, 10) 184(2) 105(100) 77(17)	$C_{17}H_{11}O_2N$	C 78.13(78.15) H 4.16(4.24) N 5.26(5.36)
3b	110.0—110.4 (benzene/hexane)	1629(C=C) 1789(C=O) 2244(CN)	7.0—7.5(8H, m, Arom. H) 8.49(1H, s, =CH-)		$C_{17}H_9O_2NCl_2$	C 61.88(61.84) H 2.78(2.75) N 4·21(4.24)
3d	187.0—188.0 (methanol)	1770(C=O) 2236(CN)	7.1—7.6(15H, m, 3×Ph)		$C_{23}H_{15}O_2N$	C 81.98(81.88) H 4.65(4.48) N 4.30(4.15)
3e	93.8—94.6 (diethyl ether/light petroleum)	1627(C=C) 1785(C=O) 2244(CN)	2.28(6H, s, 2×CH_3), 6.99(8H, s, Arom. H), 8.39(1H, s, =CH-)	289(M^+, 17) 119(100) 91(14)	$C_{19}H_{15}O_2N$	*m/z* 289.1079 (M, 289, 1103)

Table 4. (Continued 1)

Compd	Mp θ_m/°C	IR[a] cm^{-1}	^{1}H and ^{13}C NMR[b] δ	MS m/z (rel int)	Analysis Formula	Found (Calcd)
4e	184.2—184.7 (methanol)	1644 (C=C) 1685 (C=O) 1754 (C=O) 3300—3600 (NH_2)	2.31(6H, s, 2×CH_3), 6.50(1H, br. s, NH_2), 7.17(8H, s, Arom. H), 7.69(1H, br. s, NH_2), 8.70(1H, s, =CH-)		$C_{19}H_{17}O_3N$	C 74.26 (74.25) H 5.75 (5.58) N 4.66 (4.56)
5a	104.5—105.5 (methanol)	1788 (C=O) 2232 (CN)	2.88(1H, d, J=13.8 Hz, CH_2), 3.00 (1H, d, J=13.8 Hz, CH_2), 6.15(1H, s, -CH=), 6.8—7.6(20H, m, 4×Ph)	441 (M^+, 3) 397 (69) 306 (100) 217 (59) 167 (76) 105 (41) 77 (38)	$C_{31}H_{23}O_2N$	m/z 441.1734 (M, 441.1729) C 84.36 (84.33) H 5.21 (5.25) N 3.10 (3.17)
6e	273.7—274.7 (chloroform)	1648 (C=O) 2224 (CN)	2.29(6H, s, 2×CH_3), 3.43(1H, br. s, OH), 7.17(8H, s, Arom. H), 9.45(1H, br. s, NH)		$C_{19}H_{16}O_2N_2$	C 75.17 (74.98) H 5.29 (5.30) N 9.29 (9.21)
6f	185.7—186.2 (chloroform)	1606 (C=C) 1651 (C=O) 2212 (CN) 3100—3500 (NH and OH)	3.72(6H, s, 2×OCH_3), 6.7—7.3(8H, m, Arom. H), 9.50(2H, br. s, NH and OH)		$C_{19}H_{16}O_4N_2$	C 67.57 (67.85) H 4.76 (4.80) N 8.19 (8.33)
6g	210.0—211.0 (chloroform)	1647 (C=O) 2244 (CN) 3000—3600 (NH and OH)	3.71(3H, s, OCH_3), 6.8—7.5(9H, m, Arom. H), 9.54(2H, br. s, NH and OH)		$C_{18}H_{14}O_3N_2$	C 70.41 (70.58) H 4.57 (4.61) N 9.04 (9.15)
6h	over 300 (methanol)	1690 (C=O) 2228 (CN) 3000—3500 (NH)	6.9—7.7(13H, m, Arom. H), 10.11(1H, br. s, NH)	350 (M^+, 100) 321 (15) 222 (66) 195 (70)	$C_{23}H_{14}O_2N_2$	C 78.70 (78.84) H 4.05 (4.03) N 7.95 (8.00)
7e	213.4—214.4 (benzene)	1618 (C=C) 1654 (C=O) 3200—3600 (NH_2 and OH)	2.30(6H, s, 2×CH_3), 5.35(1H, br. s, OH), 6.63(1H, br. s, NH_2), 6.9—7.4(8H, m, Arom. H), 7.54(1H, br. s, NH_2), 8.28(1H, br. s, NH)	322 (M^+, 68) 279 (51) 262 (19) 193 (100) 179 (84)	$C_{19}H_{18}O_3N_2$	m/z 322.1312 (M, 322.1317)
8a	103.5—104.5 (benzene/hexane)	1716 (C=O) 2232 (CN) 3100—3500 (NH)	2.85(1H, d, J=13.8 Hz, CH_2), 2.95(1H, d, J=13.8 Hz, CH_2), 6.23(1H, s, =CH-), 6.9—7.5 (20H, m, 4×Ph), 8.23(1H, br. s, NH)	440 (M^+, 7) 397 (98) 306 (100) 217 (53) 167 (76)	$C_{31}H_{24}ON_2$	m/z 440.1874 (M, 440.1889)

Table 4. (Continued 2)

Compd	Mp θ_m/°C	IR[a] cm^{-1}	^{1}H and ^{13}C NMR[b] δ	MS *m/z* (rel int)	Analysis Formula	Found (Calcd)
8e	121.0—122.0 (benzene)	1715 (C=O) 2232 (CN) 3200—3500 (NH)	2.25 (3H, s, CH_3), 2.27 (6H, s, 2× CH_3), 2.38 (3H, s, CH_3), 2.87 (2H, br. s, CH_2), 6.11 (1H, s, =CH-), 6.8—7.3 (16H, m, Arom. H), 8.72 (1H, br. s, NH)		$C_{35}H_{32}ON_2$	C 84.35 (84.64) H 6.45 (6.50) N 5.59 (5.64)
8f	162.8—163.8 (benzene/hexane)	1720 (C=O) 2232 (CN) 3200—3500 (NH)	2.83 (1H, d, J=13.2 Hz, CH_2), 2.97 (1H, d, J=13.2 Hz, CH_2), 3.69 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 6.11 (1H, s, =CH-), 6.6—7.5 (16H, m, Arom. H), 8.93 (1H, br. s, NH)	560 (M^+, 62) 517 (100) 396 (86) 277 (80) 227 (63) 121 (34)	$C_{35}H_{32}O_5N_2$	*m/z* 560.2388 (M, 560.2311)
8g	224.1—225.1 (benzene)	1716 (C=O) 2228 (CN) 3100—3500 (NH)	2.82 (2H, br. s, CH_2), 3.71 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 6.15 (1H, s, =CH-), 6.6—7.6 (18H, m, Arom. H), 8.27 (1H, br. s, NH)		$C_{33}H_{28}O_3N_2$	C 79.26 (79.18) H 5.61 (5.64) N 5.58 (5.60)
9a	84.1—85.1 (benzene)	1227 (C-O-C) 1702 (C=O) 1740 (C=O) 2240 (CN) 3100—3600 (NH_2)	2.17 (3H, s, OAc), 2.8—4.0 (3H, m, CH_2 -CH<), 5.90 (1H, br. s, NH_2), 6.14 (1H, br. s, NH_2), 7.1—7.5 (10H, m, 2×Ph)	322 (M^+, 40) 262 (14) 239 (91) 220 (41) 195 (100) 183 (83) 165 (27) 105 (62)	$C_{19}H_{18}O_3N_2$	*m/z* 322.1311 (M, 322.1317)
9b	169.7—170.1 (benzene/hexane)	1209 (C-O-C) 1705 (C=O) 1745 (C=O) 2244 (CN) 3100—3600 (NH_2)	2.16 (3H, s, OAc), 2.8—3.9 (3H, m, CH_2-CH<), 6.25 (2H, br. s, NH_2), 7.1—7.4 (8H, m, Arom. H)		$C_{19}H_{16}O_3N_2Cl_2$	C 58.45 (58.33) H 4.21 (4.12) N 7.00 (7.16)

a) All compounds were measured in $CHCl_3$ except for **6g** and **6h** (KBr disk). b) Compounds (**6e**—**g**) were dissolved in DMSO-d_6, others were dissolved in $CDCl_3$.

acetic acid (25 cm^3), manganese(III) acetate (3—6 mmol) was added. When the color of the solution turned from brown to transparent, the reaction was stopped and then the solvent was removed in vacuo. After a work-up, **15** and **16** were obtained.

Diethyl (2,2-Diphenylethenyl)malonate (15): Colorless liquid; IR ($CHCl_3$) 1726 (C=O); ^1H NMR (CCl_4) δ=1.25 (6H, t, J=7.2 Hz, 2×CH_3), 4.00 (1H, d, J=9.6 Hz, >CH–), 4.14 (4H, q, J=7.2 Hz, 2×CH_2), 6.21 (1H, d, J=9.6 Hz, =CH–), and 7.0-7.5 (10H, m, 2×Ph); MS m/z (rel intensity), 338 (M^+, 14), 266 (13), 191 (100), 165 (19), and 115 (24).

2-Ethoxycarbonyl-4,4-diphenyl-2-buten-4-olide (16): Colorless needles (from ethanol), mp 108—109 °C (lit,[3e] mp 107.9—109.4 °C).

Oxidation of Diethyl (2,2-Diphenylethenyl)malonate (15) with Manganese(III) Acetate. A mixture of **15** (0.5 mmol) and manganese(III) acetate (1 mmol) was heated under reflux in acetic acid (25 cm^3) and worked-up using the method described above, providing **16** in the yields shown in Table 3.

The authors wish to thank Dr. Teruyosi Marunaka of the Taiho Pharmaceutical Co., Ltd., Tokushima, for his kind arrangement for the measurements of the mass and ^{13}C NMR spectra. Thanks are also due to Associate Professor Akira Mori of the Research Institute of Industrial Science, Kyushu University, and Dr. Hiromichi Matsuura of the Wakunaga Pharmaceutical Co., Ltd., Hiroshima, for their arrangement for the measurements of the mass spectra. The present work was supported by a Grant-in-Aid for Encouragement of Young Scientists No. 60740282 from the Ministry of Education, Science and Culture (1985).

References

1) a) J. B. Bush, Jr. and H. Finkbeiner, *J. Am. Chem. Soc.*, **90**, 5903 (1968); b) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 5905 (1968); c) W. E. Fristad and J. R. Peterson, *J. Org. Chem.*, **50**, 10 (1985); d) J. A. Norman, C. B. Thomas, and M. J. Burrow, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1087.

2) a) N. Ito, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **56**, 3527 (1983); b) W. E. Fristad and S. S. Hershberger, *J. Org. Chem.*, **50**, 1026 (1985).

3) a) E. J. Corey and M. Kang, *J. Am. Chem. Soc.*, **106**, 5384 (1984); b) W. E. Fristad, J. R. Peterson, and A. B. Ernst, *J. Org. Chem.*, **50**, 3143 (1985); c) A. B. Ernst and W. E. Fristad, *Tetrahedron Lett.*, **26**, 3761 (1985); d) E. J. Corey and A. W. Gross, *Tetrahedron Lett.*, **26**, 4291 (1985); e) N. Fujimoto, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **59**, 3161 (1986).

4) a) H. Nishino, *Bull. Chem. Soc. Jpn.*, **58**, 1922 (1985); b) E. I. Heiba and R. M. Dessau, *J. Org. Chem.*, **39**, 3456 (1974).

5) H. Nishino, *Bull. Chem. Soc. Jpn.*, **58**, 217 (1985).

6) a) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966); b) T. Aratani and M. J. S. Dewar, *ibid.*, **88**, 5479 (1966); c) P. J. Andrulis, Jr. and M. J. S. Dewar, *ibid.*, **88**, 5483 (1966); d) S. A. Zonis and Y. I. Kornilova, *Zhur. Obshchei Khim.*, **20**, 1252 (1950); *Chem. Abstr.*, **45**, 10196e (1951); e) S. A. Zonis and A. G. Pesina, *J. Gen. Chem., USSR*, **20**, 1223 (1950); *Chem. Abstr.*, **46**, 3496i (1952).

7) B. B. Snider, R. Mohan, and S. A. Kates, *J. Org. Chem.*, **50**, 3659 (1985).

8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 4th ed, John Wiley & Sons, Inc., New York (1980), pp. 736—744.

9) L. W. Hessel and C. Romers, *Recl. Trav. Chim. Pays-Bas*, **88**, 545 (1969).

10) E. I. Heiba, R. M. Dessau, and P. G. Rodewald, *J. Am. Chem. Soc.*, **96**, 7977 (1974).

11) G. I. Nikishin, M. G. Vinogradov, and T. M. Fedorova, *J. Chem. Soc., Chem. Commun.*, **1973**, 693.

12) T. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry," Academic Press. Inc., New York (1977).

13) O. G. Backeberg and J. L. C. Marais, *J. Chem. Soc.*, **1945**, 803.

14) W. T. Nauta, M. J. Ernsting, and A. C. Faber, *Recl. Trav. Chim. Pays-Bas*, **60**, 915 (1941).

15) M. Bösler, *Ber.*, **14**, 328 (1881).

16) B. Danieli, F. Ronchetti, and G. Russo, *Chem. Ind. (London)*, **1973**, 1067.