October, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 3161—3168 (1986)* 3161

Reaction of Olefins with Malonic Acid Derivatives in the Presence of Manganese(III) Acetate

Noriyuki Fujimoto, Hiroshi Nishino, and Kazu Kurosawa*
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860

(Received April 15, 1986)

The reaction of methylmalonic acid with mono- and disubstituted olefins in the presence of manganese(III) acetate yielded 2-carboxy-2-methyl-4-butanolides in moderate to good yields. The reactions of bromomalonic acid and chloromalonic acid with a variety of olefins gave 2-halo-4-butanolides and/or 2-buten-4-olides. The reaction of ethyl hydrogen malonate with olefins in the presence of manganese(III) acetate yielded 2-ethoxycarbonyl-2-buten-4-olides, 2-ethoxycarbonyl-2-ethenyl-4-butanolide, 2,7-dioxaspiro[4.4]nonane-1,6-diones, 2-ethoxycarbonyl-4-butanolide, and ethyl 3-butenoate. These reactions can be accounted for in terms of a free-radical mechanism involving substituted dicarboxymethyl radicals.

The formation of γ-lactones is the most characteristic feature in the reaction of manganese(III) acetate with olefins.[1] In previous publications[2,3] it was described how the reaction of olefins with malonic acid in the presence of manganese(III) acetate yielded mainly 2,7-dioxaspiro[4.4]nonane-1,6-diones. We have continued the investigation into the reaction of olefins with malonic acid derivatives in order to obtain mono-γ-lactones rather than spirodi-γ-lactones because the former are encountered more frequently in synthetic organic chemistry. Therefore the reactions of methylmalonic acid, bromomalonic acid, chloromalonic acid, and ethyl hydrogen malonate with a variety of olefins in the presence of manganese(III) acetate were examined and the results are described in this paper.

Results and Discussion

Methylmalonic Acid. When a mixture of 1,1-diphenylethene (**1a**), methylmalonic acid, and manganese(III) acetate[4,5] in a molar ratio of 1 : 1 : 2 in AcOH was heated at 100 °C, 2-carboxy-2-methyl-4,4-diphenyl-4-butanolide (**2a**) was obtained as a sole product. The maximum yield was attained when the molar ratio was 1 : 1.2 : 2.4, but in this case a small amount of decarboxylated compound (**3a**) was also obtained. The reaction at 70 °C gave **3a** and 4,4-diphenyl-4-butanolide (**4**) in prolonged reaction time. Hereafter, we conducted all the reactions at 100 °C. The effects of additives such as Ac_2O and KOAc were next examined but neither showed any appreciable influence on the yield. The reaction was also carried out under an atmosphere of nitrogen, but it did not show any significant change either in the products or in the yield. The reactions of 1,1-bis(4-methoxyphenyl)ethene (**1b**), 1,1-bis(4-methylphenyl)ethene (**1c**), 2-phenylpropene (**1e**), acenaphthylene (**1f**), styrene (**1g**), methylenecyclohexane (**1h**), and 1-octene (**1i**) gave the corresponding 2-carboxy-2-methyl-4-butanolides (**2b**, **c**, **e—i**) in moderate to good yields under similar reaction conditions. In the case of **1f**, an acetoxy acid (**5**) was obtained together with **2f** and **3f**. The **2f** and **5** were isolated as their methyl esters. The reactions of 1,1,2-triphenylethene, phenanthrene, chalcone, and (*Z*)-α-acetoxystilbene did not

Table 1. The Reaction of Olefins (**1a—c**, **e—i**) with Methylmalonic Acid in the Presence of Manganese(III) Acetate in a Molar Ratio of 1:1.2:2.4 in AcOH at 100°C

Entry	Olefin	Time min	Recovery %	Product (yield/%)[a]		Stereoisomer ratio
1[b]	**1a**	2.5	9	**2a**(62)		
2	**1a**	4		**2a**(78)	**3a**(3)	
3[c]	**1a**	14 days			**3a**(81) **4**(5)	
4[d]	**1a**	3.5	4	**2a**(72)		
5[e]	**1a**	3.5	4	**2a**(74)	**3a**(3)	
6[f]	**1a**	4.5		**2a**(76)		
7	**1b**	3.5		**2b**(70)		
8	**1c**	3		**2c**(88)		
9	**1e**	3.5		**2e**(68)[g]		58 : 42
10	**1f**	3	2	**2f**(13)[g]	**3f**(21) **5**(11)	100 : 0 for **2f** 86 : 14 for **3f**
11	**1g**	2.5		**2g**(48)[g]		54 : 46
12	**1h**	10		**2h**(56)		
13	**1i**	2.5		**2i** (30)[g]		63 : 37
14[h]	**1i**	6		**2i** (42)[g,i]		55 : 45

a) Isolated yields based on olefin added. b) A molar ratio of olefin: methylmalonic acid: Mn(III) was 1 : 1 : 2. c) At 70°C. d) Ac_2O (4.8 molar equivalents) was added. e) KOAc (2.4 molar equivalents) was added. f) Under N_2 atmosphere. g) Isolated as a methyl ester. h) **1i**: methylmalonic acid: Mn(III) was 10 : 1 : 2. i) Yield based on Mn(III) added.

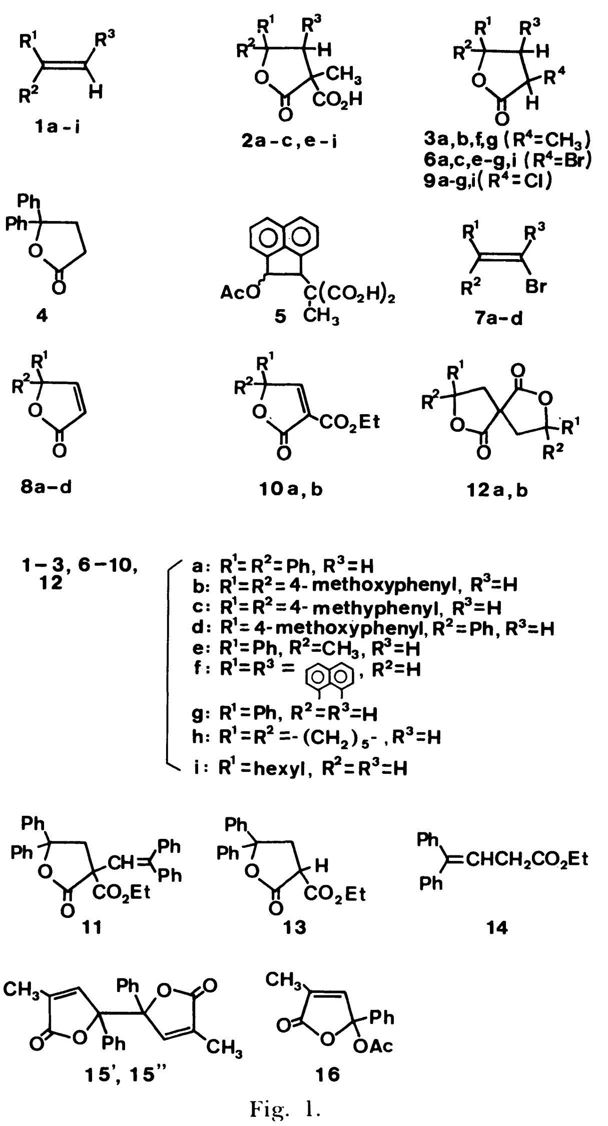


Fig. 1.

take place and the starting olefins were recovered. The 2-carboxy-2-methyl-4-butanolides obtained from **1e**, **g**, **i** were found to be a mixture of two diastereoisomers, their ratio being estimated by the ^{1}H NMR spectra or isolated yields. The stereochemistry of these lactones, however, could not be determined.

Bromomalonic Acid. When a mixture of **1a**, bromomalonic acid, and manganese(III) acetate in a molar ratio of 1 : 1.5 : 3 was heated at 100 °C, 2-bromo-4,4-diphenyl-4-butanolide (**6a**) was obtained together with 2-bromo-1,1-diphenylethene (**7a**). Similarly, **1e**, **1f**, and **1g** gave the corresponding 4-butanolides (**6e**—**g**). The olefin **1b** and 1-(4-methoxyphenyl)-1-phenylethene (**1d**), on the other hand, yielded 4,4-bis(4-methoxyphenyl)-2-buten-4-olides (**8b**) and 4-(4-methoxyphenyl)-4-phenyl-2-buten-4-olide (**8d**), respectively. The reaction of **1c** with bromomalonic acid-manganese(III) acetate gave 4,4-bis(4-methylphenyl)-2-buten-4-olide (**8c**) together with a small amount of 2-bromo-4,4-bis(4-methylphenyl)-4-butanolide (**6c**). These 2-bromo-4-butanolides (**6e**—**g**) consisted of two diastereoisomers which could be separated on TLC. The stereochemistry of each pair, however, could not be determined.

Chloromalonic Acid. The reaction of the olefins with chloromalonic acid-manganese(III) acetate gave results similar to those of bromomalonic acid except for the fact that the 2-chloro-4-butanolides (**9a**—**g**, **i**) are fairly stable.

Ethyl Hydrogen Malonate. When **1a** was oxidized with a mixture of ethyl hydrogen malonate and manganese(III) acetate in AcOH, it gave five products, i.e. 2-ethoxycarbonyl-4,4-diphenyl-2-buten-4-olide (**10a**), 2-ethoxycarbonyl-2-(2,2-diphenylethenyl)-4,4-diphenyl-4-butanolide (**11**), 3,3,8,8-tetraphenyl-2,7-dioxaspiro[4.4]-nonane-1,6-dione (**12a**), 2-ethoxycarbonyl-4,4-diphenyl-4-butanolide (**13**), and ethyl 4,4-diphenyl-3-butenoate

Table 2. Reaction of Olefins (**1a**—**g**, **i**) with Bromomalonic Acid and Chloromalonic Acid in the Presence of Manganese(III) Acetate in a Molar Ratio of 1 : 1.5 : 3 in AcOH at 100 °C

Entry	Olefin	Malonic acid	Time / min	Product (yield/%)[a]			Stereoisomer ratio
1	**1a**	Br	3	**6a**(68)	**7a**(3)		
2	**1a**	Cl	3	**9a**(82)			
3	**1b**	Br	4		**7b**(6)	**8b**(82)	
4	**1b**	Cl	3	**9b**(19)		**8b**(63)	
5	**1c**	Br	3.5	**6c**(4)	**7c**(5)	**8c**(69)	
6	**1c**	Cl	4	**9c**(74)			
7	**1d**	Br	3.5		**7d**(3)	**8d**(67)	
8	**1d**	Cl	3.5	**9d**(36)		**8d**(30)	Not determined
9	**1e**	Br	4	**6e**(54)			59 : 41
10	**1e**	Cl	4	**9e**(46)			54 : 46
11	**1f**	Br	4.5	**6f**(40)			68 : 32
12	**1f**	Cl	3	**9f**(32)			78 : 22
13	**1g**	Br	4	**6g**(28)			68 : 32
14	**1g**	Cl	4	**9g**(28)			75 : 25
15	**1i**	Cl	5.5	**9i**(6)			67 : 33

a) Isolated yields based on olefin added.

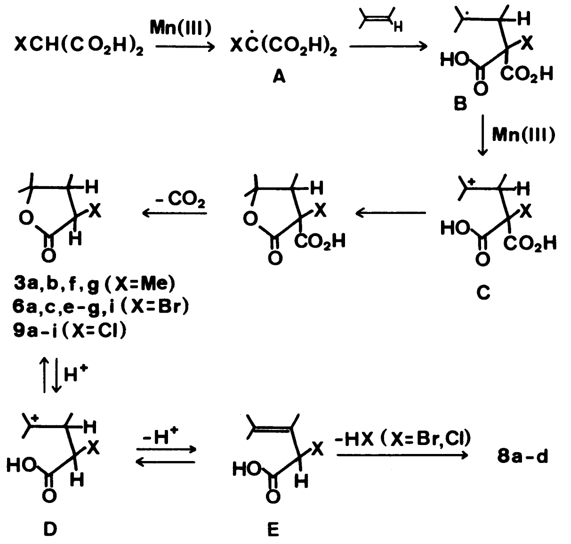
Table 3. Reaction of **1a** with Ethyl Hydrogen Malonate in the Presence of Manganese(III) Acetate in Boiling AcOH

Entry	Molar ratio[a]	Time min	Recovery %	Product (yield/%)[b] **10a**	**11**	**12a**	**13**	**14**
1	2 : 1 : 4	15	9		57	8		17
2	2 : 1.2 : 4.8	300		3	69	4		12
3	1 : 1 : 2	3	3		17	6	12	12
4	1 : 1 : 3	6		3	45	17		7
5	1 : 1 : 4	110		4	32	22		
6	1 : 1 : 5	390		8	24	8		
7	1 : 2 : 5	80		20	27	8		
8	1 : 3 : 5	35		15	21	8		
9	1 : 4 : 5	20		13	16	6		
10	1 : 5 : 6	22		28	12	6		
11	1 : 6 : 7	21		29	9	7		
12[c]	1 : 6 : 7	22		25	12	11		
13	1 : 6 : 10	24		23	8	6		
14	1 : 6 : 12	32		24	3	3		
15	1 : 8 : 9	17		25	9	6		
16	1 : 10 : 11	13		23	2	7		

a) **1a**: ethyl hydrogen malonate: Mn(III). b) Isolated yields based on **1a** added. c) Ac_2O (16 molar equivalents) was added.

(**14**). The yield of **10a** was slightly improved with the increase of the amounts of ethyl hydrogen malonate and manganese(III) acetate at the expense of the yields of **11** and **12a**. In the reaction at a molar ratio of 1:1:2, the compounds **13** and **14** were formed in minor quantity along with **11** and **12a**. When the molar ratio was 2:1.2:4.8, **11** became the major product (Table 3, Entry 2). Addition of Ac_2O to the reaction mixture showed little effect on the product distribution. Similarly **1b** yielded **10b** (31%) and **12b** (8%).

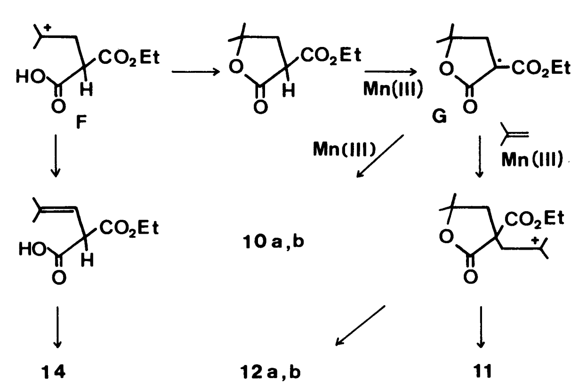
The reaction of olefins with malonic acid derivatives-manganese(III) acetate proceeded smoothly at 100 °C in a few minutes to give substituted 4-butanolides and 2-buten-4-olides. As already described for the reactions of malonic acid[2] and malonamide[6] with olefin in the presence of manganese(III) acetate, the first step in the reaction of substituted malonic acid must be the formation of substituted malonic acid radical A as the result of the interaction between the malonic acid and manganese(III) acetate. The radical A reacts with an olefin to form a secondary or tertiary carbon radical B which is oxidized to the corresponding carbonium ion C. Upon cyclization followed by deprotonation, the carbonium ion C gives a 2-carboxy-4-butanolide which can be decarboxylated, while some 2-halo-4-butanolides are dehydrohalogenated to give 2-buten-4-olides. In fact, when 2-carboxy-2-methyl-4-butanolides (**2a, b, g**) were heated in AcOH, they gave the decarboxylated products (**3a, b, g**) in excellent yields. These are shown in Scheme 1. It should be pointed out that the substituted dicarboxymethyl radicals regiospecifically add to the less hindered site on the C=C bond. It should be noted also that the reactions of 4-methoxyphenyl (**1b** and **1d**) and 4-methylphenyl-substituted olefin (**1c**) with halomalonic acid tend to give 2-buten-4-olides rather than 2-halo-4-butanolides,



Scheme 1. Possible mechanisms for the formation of γ-lactones.

and some 2-bromo-4-butanolides having a 4-methoxyphenyl group also tend to give 2-buten-4-olides on spontaneous dehydrobromination. An attempt to dehydrohalogenate 4-phenyl-substituted 2-halo-4-butanolides with base failed to yield the corresponding 2-buten-4-olides. These facts may suggest that the carbonium ion D which is in equilibrium with 2-halo-4-butanolides suffered from deprotonation at the adjacent carbon to give 4,4-diaryl-2-halo-3-butenoic acid (E). The latter lactonized to give 2-buten-4-olides. In fact, **6a** was converted to **8a** in a 95% yield on heating in AcOH for 1 h. The formation of bromoethenes (**7a—d**) indicates that Br^- ion or Br• radical was produced in the reaction of bromomalonic acid with manganese(III) acetate.

The reactions of ethyl hydrogen malonate with olefins in the presence of manganese(III) acetate are different from those of methyl-, bromo-, and chloromalonic acid. The reaction was previously reported by Fristad[3] and Corey[7] who both obtained 2-ethoxycarbonyl-4-butanoldie alone. When we repeated the reaction of **1a** with ethyl hydrogen malonate-manganese(III) acetate, it was found that several other products were also formed and the product distribution depended largely on the molar ratio of olefin and ethyl hydrogen malonate as shown in Table 3. The reaction of **13** with manganese(III) acetate gave **10a** (24%), and the reaction of **13** with a mixture of **1a** and manganese(III) acetate yielded **11** (79%) and **12a** (5%). Thus the pathway for the formation of **10a**, **11**, **12a**, and **14** can be depicted as shown in Scheme 2. Our results indicate that the reaction proved to be useful not only for the preparation of 2-ethoxycarbonyl-4-butanolides but also for the preparations of 2-ethoxycarbonyl-2-buten-4-olides and 2-vinyl-4-butanolides.



Scheme 2. Pathways for the reaction of olefins with ethyl hydrogen malonate in the presence of manganese(III) acetate.

The formation of 2-carboxy-2-methyl-4-butanolides (**2a**—**c**, **e**—**i**) by the reaction of an olefin with methylmalonic acid-manganese(III) acetate led us to investigate the reaction of acetylene with these reagents, since it might give rise to 2-methyl-2-buten-4-olides. The reaction of phenylacetylene with methylmalonic acid-manganese(III) acetate, however, yielded a mixture of isomeric 2,2′-dimethyl-4,4′-diphenyl-4,4′-bis(2-buten-4-olide) (**15′** and **15″**) (25%), and 4-acetoxy-2-methyl-4-phenyl-2-buten-4-olide (**16**) (7%). It was also observed that one of the isomers (**15″**) was converted to the other (**15′**) during recrystallization.

2-Methyl-4-butanolides and 2-chloro-4-butanolides were previously obtained by the reaction of an olefin with manganese(III) acetate in propionic acid[8] and in chloroacetic acid,[9] respectively, but in poor yields. The reaction of olefins with methylmalonic acid in the presence of manganese(III) acetate is a much better method for the preparation of 2-alkyl-4-butanolides, but for the preparation of 2-chloro-4-butanolides it was reported that the ruthenium(II)-catalyzed reaction of olefins with trimethylsilyl α-polychlorinated carboxylates gave γ-lactones in fairly good yields.[10] 2-Bromo-4-butanolides (**5a**—**c**, **e**—**i**) have not been synthesized before, therefore our reaction can be useful for the preparation of these compounds.

Experimental

Measurements. All the ^{1}H NMR spectra were recorded with a Hitachi Perkin-Elmer R-24 spectrometer (60 MHz) with tetramethylsilane as the internal reference. The IR spectra were measured in chloroform solution on a JASCO A-102 infrared spectrometer. The mass spectra were obtained with a Hitachi M-80B, a JEOL JMS-DX 300, and a JEOL JMS-OISG mass spectrometer. The melting points were determined with a Yanagimoto micromelting point apparatus and were not corrected.

Materials. The olefins (**1a**—**e**, **h**),[2] 1,1-bis(4-methylphenyl)-ethene (**1c**),[11] 1-(4-methoxyphenyl)-1-phenylethene (**1d**),[12] manganese(III) acetate,[4] bromomalonic acid,[13] and chloromalonic acid[13] were prepared by the method described in the literature. Acenaphthylene (**1f**), styrene (**1g**), and 1-octene (**1i**) were purchased from Wako Pure Chemical Industries, Ltd. Methylmalonic acid was commercially available from Aldrich Chemical Co.

Reaction of Olefins with Methylmalonic Acid in the Presence of Manganese(III) Acetate. To a heated solution of olefin (1 mmol) and methylmalonic acid (1.2 mmol) in AcOH (30 cm^3), manganese(III) acetate (2.4 mmol) was added. The solution was heated at 100 °C for the period of time shown in Table 1. After adding water (100 cm^3), the mixture was extracted with benzene. The solvent was removed under reduced pressure. When the resulting crude product was crystalline, the product was recrystallized from benzene and the filtrate was separated on TLC with benzene or chloroform as the developing solvent. In other cases, the product was separated on TLC with chloroform as developing solvent. In the cases of **2e**, **g**, **i**, the stereoisomers were further separated on TLC with 20—30% ether/light petroleum as the developing solvent after methylation with diazomethane.

Reaction Products of 1,1-Diphenylethene (1a) with Methylmalonic Acid-Mn(III). 2-Carboxy-2-methyl-4,4-diphenyl-4-butanolide (2a): Colorless plates (from benzene); mp 161.2—162.1 °C; IR 3600—2400 (COOH), 1777 (-COO-), and 1714 cm^{-1} (COOH); ^{1}H NMR (DMSO-d_6) δ=1.25 (3H, s, CH_3), 3.06 (1H, d, J=1.6 Hz, H-3), 3.55 (1H, d, J=12.6 Hz, H-3), 7.0 (1H, br. s, COOH), and 7.1—7.6 (10H, m, ar. H). Found: C, 72.75; H, 5.36%. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%.

2-Methyl-4,4-diphenyl-4-butanolide (3a): Colorless plates (from methanol); mp 120.2—120.7 °C; IR 1770 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=1.14 (3H, d, J=6.6 Hz, CH_3), 2.1—3.4 (3H, m, H-2 and 2×H-3), and 7.1—7.6 (10H, m, ar. H). Found: C, 80.90; H, 6.42%. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39%.

4,4-Diphenyl-4-butanolide (4): Colorless microcrystals (from ethanol); mp 89.9—91.1 °C (lit,[14] mp 87—90 °C).

Reaction Product of 1,1-Bis(4-methoxyphenyl)ethene (1b) with Methylmalonic Acid-Mn(III). 2-Carboxy-4,4-bis(4-methoxyphenyl)-2-methyl-4-butanolide (2b): Colorless needles (from benzene); mp 140.0—140.7 °C; IR 3600—2400 (COOH), 1773 (-COO-), and 1715 cm^{-1} (COOH); ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, s, CH_3), 2.83 (1H, d, J=13.2 Hz, H-3), 3.53 (1H, d, J=13.2 Hz, H-3), 3.71 (3H, s, OCH_3), 3.75 (3H, s,

OCH_3), 6.6—7.5 (8H, m, ar. H), and 10.14 (1H, br. s, COOH). Found: C, 67.51; H, 5.37%. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66%.

Reaction Product of 1,1-Bis(4-methylphenyl)ethene (1c) with Methylmalonic Acid-Mn(III). 2-Carboxy-2-methyl-4,4-bis(4-methylphenyl)-4-butanolide (2c): Colorless needles (from benzene); mp 148.3—149.2 °C; IR 3600—2400 (COOH), 1775 (-COO-), and 1717 cm^{-1} (COOH); ^1H NMR ($CDCl_3$) δ=1.34 (3H, s, CH_3), 2.27 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.87 (1H, d, J=13.2 Hz, H-3), 3.51 (1H, d, J=13.2 Hz, H-3), 6.9—7.5 (8H, m, ar. H), and 10.53 (1H, br. s, COOH). Found: C, 74.10; H, 6.30%. Calcd for $C_{20}H_{20}O_4$: C, 74.06: H, 6.21%.

Reaction Product of 2-Phenylpropene (1e) with Methylmalonic Acid-Mn(III). Methyl Ester of 2-Carboxy-2-methyl-4-phenyl-4-pentanolide (2e′): From the upper fraction on TLC (developing solvent: 30% ether/light petroleum); liquid; IR 1771 (-COO-) and 1735 cm^{-1} ($COOCH_3$); ^1H NMR ($CDCl_3$) δ=1.35 (3H, s, CH_3), 1.74 (3H, s, CH_3), 2.47 (1H, d, J=13.2 Hz, H-3), 3.09 (1H, d, J=13.2 Hz, H-3), 3.80 (3H, s, $COOCH_3$), 7.31 (5H, s, Ph). Found: m/z 248.1065. Calcd for $C_{14}H_{16}O_4$: M, 248.1049.

Stereoisomeric Methyl Ester of 2-Carboxy-2-methyl-4-phenyl-4-pentanolide (2e″): From the lower fraction of TLC (developing solvent: 30% ether/light petroleum); colorless plates (from methanol); mp 91.7—92.2 °C; IR 1776 (-COO-) and 1736 cm^{-1} ($COOCH_3$); ^1H NMR ($CDCl_3$) δ= 1.57 (3H, s, CH_3), 1.72 (3H, s, CH_3), 2.31 (1H, d, J=13.2 Hz, H-3), 3.21 (3H, s, $COOCH_3$), 3.23 (1H, d, J=13.2 Hz, H-3), and 7.28 (5H, s, Ph). Found: C, 67.52; H, 6.40%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

Reaction Products of Acenaphthylene (1f) with Methylmalonic Acid-Mn(III). Methyl Ester of 9-Carboxy-9-methyl-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (2f): Colorless needles (from benzene/hexane); mp 115.2—115.7 °C; IR 1773 (-COO-) and 1743 cm^{-1} ($COOCH_3$); ^1H NMR ($CDCl_3$) δ=1.80 (3H, s, CH_3), 2.88 (3H, s, $COOCH_3$), 4.25 (1H, d, J=7.8 Hz, H-6b), 6.23 (1H, d, J=7.8 Hz, H-9a), and 7.0—8.0 (6H, m, ar. H). Found: C, 72.36; H, 4.94%. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%.

9-Methyl-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (3f′): From the upper fraction on TLC (developing solvent: chloroform); liquid; IR 1766 cm^{-1} (-COO-); ^1H NMR (CCl_4) δ=1.48 (3H, d, J=7.8 Hz, CH_3), 2.2—2.8 (1H, m, H-7), 3.88 (1H, t, J=6.6 Hz, H-6b), 6.02 (1H, d, J=6.6 Hz, H-9a), and 7.0—8.0 (6H, m, ar. H). Found: m/z 224.0863. Calcd for $C_{15}H_{12}O_3$: M, 224.0837.

Stereoisomeric 9-Methyl-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (3f″): From the lower fraction on TLC (developing solvent: chloroform); colorless plates (from benzene/hexane); mp 123.9—124.2 °C; IR 1763 cm^{-1} (-COO-); ^1H NMR ($CDCl_3$) δ=1.29 (3H, d, J=7.8 Hz, CH_3), 3.20 (1H, dq, J=7.8 and 10.8 Hz, H-7), 4.50 (1H, dd, J=6.6 and 10.8 Hz, H-6b), 6.16 (1H, d, J=6.6 Hz, H-9a), and 7.1—8.0 (6H, m, ar. H). Found: C, 80.31; H, 5.43%. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39%.

1-Acetoxy-2-[1,1-bis(methoxycarbonyl)ethyl]acenaphthene (Dimethyl Ester of 5): Liquid; IR 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.23 (3H, s, CH_3), 2.07 (3H, s, OAc), 3.66 (3H, s, $COOCH_3$), 3.80 (3H, s, $COOCH_3$), 4.57 (1H, d, J=1.8 Hz, H-2), 6.65 (1H, d, J=1.8 Hz, H-1), and 7.1—7.9 (6H, m, ar. H). Found: m/z 356.1279. Calcd for $C_{20}H_{20}O_6$: M, 356.1260.

Reaction Products of Styrene (1g) with Methylmalonic Acid-Mn(III). Methyl Ester of 2-Carboxy-2-methyl-4-phenyl-4-butanolide (2g′): From the upper fraction on TLC (developing solvent: 30% ether/light petroleum); colorless plates (from benzene/hexane); mp 81.2—81.6 °C; IR 1778 (-COO-) and 1736 cm^{-1} ($COOCH_3$); ^1H NMR (CCl_4) δ=1.49 (3H, s, CH_3), 1.99 (1H, dd, J=10.2 and 13.8 Hz, H-3), 3.04 (1H, dd, J=6.0 and 13.8 Hz, H-3), 3.78 (3H, s, $COOCH_3$), 5.40 (1H, dd, J=6.0 and 10.2 Hz, H-4), and 7.33 (5H, s, ar. H). Found: C, 66.69; H, 5.97%. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02%.

Stereoisomeric Methyl Ester of 2-Carboxy-2-methyl-4-phenyl-4-butanolide (2g″): From the lower fraction on TLC (developing solvent: 30% ether/light petroleum); liquid; IR 1778 (-COO-) and 1741 cm^{-1} ($COOCH_3$); ^1H NMR (CCl_4) δ=1.50 (3H, s, CH_3), 2.45 (1H, dd, J=7.2 and 12.6 Hz, H-3), 2.67 (1H, dd, J=8.4 and 12.6 Hz, H-3), 3.62 (3H, s, $COOCH_3$), 5.38 (1H, dd, J=7.2 and 8.4 Hz, H-4), and 7.25 (5H, s, ar. H). Found: m/z 234.0876; Calcd for $C_{13}H_{14}O_4$: M, 234.0892.

Reaction Product of Methylenecyclohexane (1h) with Methylmalonic Acid-Mn(III). 3-Carboxy-3-methyl-1-oxaspiro[4.5]decan-2-one (2h): Colorless microcrystals (from benzene); mp 147.8—148.3 °C; IR 3600—2400 (COOH), 1762 (-COO-), and 1714 cm^{-1} (COOH); ^1H NMR ($CDCl_3$) δ=1.0—3.0 (10H, m, 5×CH_2), 1.59 (3H, s, CH_3), 1.99 (1H, d, J=13.2 Hz, H-4), 2.72 (1H, d, J=13.2 Hz, H-4), and 11.52 (1H, s, COOH). Found: C, 62.14; H, 7.34%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

Reaction Products of 1-Octene (1i) with Methylmalonic Acid-Mn(III). Methyl Ester of 2-Carboxy-2-methyl-4-decanolide (2i′): From the upper fraction on TLC (developing solvent: 20% ether/light petroleum); liquid; bp 110—115 °C (bath temp)/0.002 mmHg (1 mmHg=133.322 Pa); IR 1771 (-COO-) and 1735 cm^{-1} ($COOCH_3$); ^1H NMR (CCl_4) δ=0.6—2.0 (13H, m, C_6H_{13}-), 1.42 (3H, s, CH_3), 1.70 (1H, dd, J=6.6 and 12.6 Hz, H-3), 2.65 (1H, dd, J=5.4 and 12.6 Hz, H-3), 3.72 (3H, s, $COOCH_3$), and 4.1—4.7 (1H, m, H-4). Found for the stereoisomeric mixture: C, 64.31; H, 9.06%. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%.

Stereoisomeric Methyl Ester of 2-Carboxy-2-methyl-4-decanolide (2i″): From the lower fraction on TLC (developing solvent: 20% ether/light petroleum); liquid; bp 110—115 °C/0.002 mmHg; IR 1771 (-COO-) and 1740 cm^{-1} ($COOCH_3$); ^1H NMR (CCl_4) δ=0.6—2.0 (13H, m, C_6H_{13}-), 1.41 (3H, s, CH_3), 2.18 (1H, dd, J=7.2 and 13.2 Hz, H-3), 2.38 (1H, dd, J=8.4 and 13.2 Hz, H-3), 3.71 (3H, s, CH_3), and 4.1—4.6 (1H, m, H-4). Found for stereoisomeric mixture: C, 64.31; H, 9.06%. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15%.

Reaction of Olefins with Bromomalonic Acid and Chloromalonic Acid in the Presence of Manganese(III) Acetate. To a heated solution of the olefin (1 or 2 mmol) and halomalonic acid (1.5 or 3 mmol) in AcOH (30 cm^3), manganese(III) acetate (3 or 6 mmol) was added. The solution was heated at 100 °C for the period of time shown in Table 2. After removal of the solvent under reduced pressure, 2M hydrochloric acid (50 cm^3) was added and the mixture was extracted with chloroform. The solvent was removed under reduced pressure and the resulting crude product was separated on TLC with benzene or chloroform as the developing solvent.

Reaction Products of 1a with Bromomalonic Acid-Mn(III). 2-Bromo-4,4-diphenyl-4-butanolide (6a): Liquid; IR 1788 cm^{-1} (-COO-); ^1H NMR (CCl_4) δ=3.06 (1H, dd, J=10.2 and 13.8 Hz, H-3), 3.51 (1H, dd, J=7.8 and 13.8

Hz, H-3), 4.35 (1H, dd, *J*=7.8 and 10.2 Hz, H-2), 7.0—7.5 (10H, m, ar. H). Found: *m/z* 316.0090, 318.0072. Calcd for $C_{16}H_{13}{}^{79}BrO_2$: M, 316.0099; $C_{16}H_{13}{}^{81}BrO_2$: M, 318.0079.

2-Bromo-1,1-diphenylethene (7a): Liquid (lit,[15] mp 42 °C).

Reaction Product of 1a with Chloromalonic Acid-Mn(III). 2-Chloro-4,4-diphenyl-4-butanolide (9a): Colorless microcrystals (from ethanol); mp 90.0—91.4 °C; IR 1789 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=2.95 (1H, dd, *J*=10.2 and 12.6 Hz, H-3), 3.51 (1H, dd, *J*=6.6 and 12.6 Hz, H-3), 4.44 (1H, dd, *J*=6.6 and 10.2 Hz, H-2), and 7.1—7.2 (10H, m, ar. H). Found: C, 70.35; H, 4.84%. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80%.

Reaction Products of 1b with Bromomalonic Acid-Mn(III). 2-Bromo-1,1-bis(4-methoxyphenyl)ethene (7b): Liquid (lit,[15] mp 80—82 °C). **4,4-Bis(4-methoxyphenyl)-2-buten-4-olide (8b):** Pale yellow needles (from ethanol); mp 133.2—134.2 °C; IR 1764 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=3.74 (6H, s, 2×OCH_3), 6.08 (1H, d, *J*=6.0 Hz, H-2), 6.7—7.3 (8H, m, ar. H), and 7.81 (1H, d, *J*=6.0 Hz, H-3). Found: C, 72.80; H, 5.47%. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44%.

Reaction Products of 1b with Chloromalonic Acid-Mn(III). 4,4-Bis(4-methoxyphenyl)-2-buten-4-olide (8b). 2-Chloro-4,4-bis(4-methoxyphenyl)-4-butanolide (9b): Liquid; IR 1788 cm^{-1} (-COO-); ^{1}H NMR (CCl_4) δ=2.88 (1H, dd, *J*=10.8 and 13.2 Hz, H-3), 3.44 (1H, dd, *J*=7.8 and 13.2 Hz, H-3), 3.75 (6H, s, 2×OCH_3), 4.27 (1H, dd, *J*=7.8 and 10.8 Hz, H-2), 6.6—7.4 (8H, m, ar. H). Found: *m/z* 332.0824, 334.0829. Calcd for $C_{18}H_{17}{}^{35}ClO_4$: M, 332.0815; $C_{18}H_{17}{}^{37}ClO_4$: M, 334.0786.

Reaction Products of 1c with Bromomalonic Acid-Mn(III). 2-Bromo-4,4-bis(4-methylphenyl)-4-butanolide (6c): Liquid; IR 1788 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=2.29 (6H, s, 2×CH_3), 2.99 (1H, dd, *J*=10.2 and 13.8 Hz, H-3), 3.45 (1H, dd, 7.8 and 13.8 Hz, H-3), 4.35 (1H, dd, *J*=7.8 and 10.2 Hz, H-2), 6.9—7.4 (8H, m, ar. H). Found: *m/z* 344.0336, 346.0412. Calcd for $C_{18}H_{17}{}^{79}BrO_2$: M, 344.0412; $C_{18}H_{17}{}^{81}BrO_2$: M, 346.0392.

2-Bromo-1,1-bis(4-methylphenyl)ethene (7c): Liquid (lit,[15] mp 55—57 °C). **4,4-Bis(4-methylphenyl)-2-buten-4-olide (8c):** Colorless needles (from methanol); mp 102.8—103.3 °C; IR 1763 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=2.32 (6H, s, 2×CH_3), 6.11 (1H, d, *J*=6.0 Hz, H-2), 7.31 (8H, s, ar. H), and 7.84 (1H, d, *J*=6.0 Hz, H-3). Found: C, 81.56; H, 6.09%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

Reaction Products of 1d with Bromomalonic Acid-Mn(III). 2-Bromo-1-(4-methoxyphenyl)-1-phenylethene (7d): Liquid (a mixture of (*E*)- and (*Z*)-isomers); ^{1}H NMR (CCl_4) δ=3.69 and 3.75 (3H, s, s, CH_3), 6.5—7.4 (10H, m, =CH- and ar. H); MS *m/z* 288, 290. **4-(4-Methoxyphenyl)-4-phenyl-2-buten-4-olide (8d):** Colorless needles (from ethanol); mp 118.6—119.6 °C; IR 1763 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=3.71 (3H, s, OCH_3), 6.06 (1H, d, *J*=5.4 Hz, H-2), 6.7—7.4 (9H, m, ar. H), 7.87 (1H, d, *J*=5.4 Hz, H-3). Found: C, 76.73; H, 5.33%. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.

Reaction Products of 1d with Chloromalonic Acid-Mn(III). 4-(4-Methoxyphenyl)-4-phenyl-2-buten-4-olide (8d). 2-Chloro-4-(4-methoxyphenyl)-4-phenyl-4-butanolide (9d): Liquid (a mixture of stereoisomers); IR 1790 cm^{-1} (-COO-); ^{1}H NMR (CCl_4) δ=2.5—3.1 (1H, m, H-3), 3.2—3.7 (1H, m, H-3), 3.69 (3H, s, OCH_3), 4.1—4.6 (1H, m, H-2), and 6.6—7.5 (9H, m, ar. H). Found: *m/z* 302.0667, 304.0692. Calcd for $C_{17}H_{15}{}^{35}ClO_3$: M, 302.0710; $C_{17}H_{15}{}^{37}ClO_3$: 304.0680.

Reaction Products of 1e with Bromomalonic Acid-Mn(III). 2-Bromo-4-phenyl-4-pentanolide (6e′): From the upper fraction on TLC (developing solvent: benzene); liquid; IR 1783 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=1.83 (3H, s, CH_3), 2.72 (1H, dd, *J*=8.4 and 13.2 Hz, H-3), 3.11 (1H, dd, *J*=8.4 and 13.2 Hz, H-3), 4.44 (1H, t, *J*=8.4 Hz, H-2), and 7.32 (5H, s, ar. H). Found: *m/z* 253.9951, 255.9910. Calcd for $C_{11}H_{11}{}^{79}BrO_2$: M, 253.9943; $C_{11}H_{11}{}^{81}BrO_2$: 255.9922.

Stereoisomeric 2-Bromo-4-phenyl-4-pentanolide (6e″): From the lower fraction on TLC (developing solvent: benzene); liquid; IR 1776 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=1.69 (3H, s, CH_3), 2.81 (1H, dd, *J*=7.2 and 13.8 Hz, H-3), 3.04 (1H, dd, *J*=7.2 and 13.8 Hz, H-3), 4.66 (1H, t, *J*=7.2 Hz, H-2), and 7.32 (5H, s, ar. H). Found: *m/z* 253.9949, 255.9954. Calcd for $C_{11}H_{11}{}^{79}BrO_2$: M, 253.9943; $C_{11}H_{11}{}^{81}BrO_2$: M, 255.9922.

Reaction Products of 1e with Chloromalonic Acid-Mn(III). 2-Chloro-4-phenyl-4-pentanolide (9e′): From the upper fraction on TLC (developing solvent: chloroform); liquid.[10]

Stereoisomeric 2-Chloro-4-phenyl-4-pentanolide (9e″): From the lower fraction on TLC (developing solvent: chloroform); liquid.[10]

Reaction Products of 1f with Bromomalonic Acid-Mn(III). 9-Bromo-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (6f′): From the upper fraction on TLC (developing solvent: chloroform); pale yellow needles (from methanol); mp 127.6—128.5 °C; IR 1777 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=4.4—4.7 (2H, m, H-6b and H-7), 6.30 (1H, d, *J*=5.4 Hz, H-9a), and 7.0—8.0 (6H, m, ar. H). Found: C, 58.14; H, 3.13%. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%.

Stereoisomeric 9-Bromo-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (6f″): From the lower fraction on TLC (developing solvent: chloroform); colorless needles (from methanol); mp 172.6—173.1 °C; IR 1785 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=4.62 (1H, dd, *J*=6.0 and 10.2 Hz, H-6b), 5.10 (1H, d, *J*=10.2 Hz, H-7), 6.26 (1H, d, *J*=6.0 Hz, H-9a), and 7.3—8.0 (6H, m, ar. H). Found: C, 58.40; H, 3.14%. Calcd for $C_{14}H_9BrO_2$: C, 58.16; H, 3.14%.

Reaction Products of 1f with Chloromalonic Acid-Mn(III). 9-Chloro-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (9f′): From the upper fraction on TLC (developing solvent: chloroform); pale yellow microcrystals (from benzene/hexane); mp 115.2—116.2 °C; IR 1782 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=4.4—4.8 (2H, m, H-6b and H-7), 6.38 (1H, d, *J*=6.0 Hz, H-9a), and 7.2—8.0 (6H, m, ar. H). Found: *m/z* 244.0254, 246.0278. Calcd for $C_{14}H_9{}^{35}ClO_2$: M, 244.0291; $C_{14}H_9{}^{37}ClO_2$: M, 246.0262.

Stereoisomeric 9-Chloro-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan-8(9*H*)-one (9f″): From the lower fraction on TLC (developing solvent: chloroform); colorless plates (from benzene); mp 192.5—193.5 °C; IR 1787 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=4.68 (1H, dd, *J*=6.0 and 10.2 Hz, H-6b), 5.10 (1H, d, *J*=10.2 Hz, H-7), 6.22 (1H, d, *J*=6.0 Hz, H-9a), 7.2—8.0 (6H, m, ar. H). Found: *m/z* 244.0293, 246.0253. Calcd for $C_{14}H_9{}^{35}ClO_2$: M, 244.0291; $C_{14}H_9{}^{37}ClO_2$: M, 246.0262.

Reaction Products of 1g with Bromomalonic Acid-Mn(III). 2-Bromo-4-phenyl-4-butanolide (6g′): From the upper fraction on TLC (developing solvent: benzene); liquid; IR 1788 cm^{-1} (-COO-); ^{1}H NMR (CCl_4) δ=2.5—2.8 (2H, m, 2×H-3), 4.43 (1H, dd, *J*=3.0 and 5.4 Hz, H-2), 5.55 (1H, dd, *J*=6.6 and 7.8 Hz, H-4), and 7.26 (5H, s, Ph). Found: *m/z* 239.9777, 241.9780: Calcd for $C_{10}H_9{}^{79}BrO_2$: M, 239.9786;

$C_{10}H_9{}^{81}BrO_2$: M, 241.9766.

Stereoisomeric 2-Bromo-4-phenyl-4-butanolide (6g″): From the lower fraction on TLC (developing solvent: benzene); liquid; IR 1788 cm^{-1} (-COO-); ^{1}H NMR (CCl_4) δ=2.1—2.7 (1H, m, H-3), 2.9—3.5 (1H, m, H-3), 4.62 (1H, dd, *J*=8.4 and 9.6 Hz, H-2), 5.37 (1H, dd, *J*=6.6 and 9.6 Hz, H-4), and 7.23 (5H, s, Ph). Found: *m/z* 239.9801, 241.9808. Calcd for $C_{10}H_9{}^{79}BrO_2$: M, 239.9786; $C_{10}H_9{}^{81}BrO_2$: M, 241.9766.

Reaction Products of 1g with Chloromalonic Acid–Mn(III). 2-Chloro-4-phenyl-4-butanolide (9g′): From the upper fraction on TLC (developing solvent: chloroform); liquid.[10]

Stereoisomeric 2-Chloro-4-phenyl-4-butanolide (9g″): From the lower fraction on TLC (developing solvent: chloroform); liquid.[10]

Reaction Products of 1i with Chloromalonic Acid–Mn(III). 2-Chloro-4-decanolide (9i′): From the upper fraction on TLC (developing solvent: benzene); liquid.[16]

Stereoisomeric 2-Chloro-4-decanolide (9i″): From the lower fraction on TLC (developing solvent: benzene); liquid.[16]

Reaction of Olefins with Ethyl Hydrogen Malonate in the Presence of Manganese(III) Acetate. To a heated solution of olefin (1 or 2 mmol) and ethyl hydrogen malonate in AcOH (30 cm^3), manganese(III) acetate was added. The solution was heated under reflux for the period of time shown in Table 3. After adding water (100 cm^3), the mixture was extracted with benzene, and the solvent was removed under reduced pressure. The resulting crude product was separated on TLC with chloroform as the developing solvent.

Reaction Products of 1a with Ethyl Hydrogen Malonate–Mn(III). 2-Ethoxycarbonyl-4,4-diphenyl-2-buten-4-olide (10a): Colorless plates (from methanol); mp 107.9—109.4 °C; IR 1782 (-COO-), 1719 (-COOEt), and 1642 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.31 (3H, t, *J*=7.2 Hz, CH_3), 4.31 (2H, q, *J*=7.2 Hz, -CH_2-), 7.28 (10H, s, 2×Ph), and 8.57 (1H, s, =CH-). Found: C, 73.87; H, 5.21%. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23%.

2-Ethoxycarbonyl-4,4-diphenyl-2-(2,2-diphenylethenyl)-4-butanolide (11): Colorless needles (from benzene); mp 279.8—281.5 °C; IR 1776 (-COO-) and 1734 cm^{-1} (COOEt); ^{1}H NMR ($CDCl_3$) δ=0.94 (3H, t, *J*=7.2 Hz, CH_3), 2.72 (1H, d, *J*=12.6 Hz, H-3), 3.28 (1H, d, *J*=12.6 Hz, H-3), 3.62 (2H, q, *J*=7.2 Hz, -OCH_2-), 6.32 (1H, s, =CH-), and 6.9—7.6 (20H, m, 4×Ph). Found: C, 80.93; H, 5.58%. Calcd for $C_{33}H_{28}O_4$: C, 81.12; H, 5.78%.

3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (12a): Colorless needles (from benzene); mp 284.5—285.0 °C (lit,[2] mp 284.5—285.0 °C).

2-Ethoxycarbonyl-4,4-diphenyl-4-butanolide (13): Colorless prisms (from benzene/hexane); mp 67.4—68.5 °C; IR 1782 (-COO-) and 1735 cm^{-1} (COOEt); ^{1}H NMR ($CDCl_3$) δ=1.17 (3H, t, *J*=7.2 Hz, CH_3), 3.0—3.8 (3H, m, -CH_2- and >CH-), 4.13 (2H, q, *J*=7.2 Hz, OCH_2-), and 7.1—7.5 (10H, m, 2×Ph). Found: *m/z* 310.1187. Calcd for $C_{19}H_{18}O_4$: M, 310.1205.

Ethyl 4,4-diphenyl-3-butenoate (14): Liquid.[17]

Reaction Products of 1b with Ethyl Hydrogen Malonate–Mn(III). 2-Ethoxycarbonyl-4,4-bis(4-methoxyphenyl)-2-buten-4-olide (10b): Liquid; IR 1781 (-COO-), 1717 (COOEt), and 1640 cm^{-1} (C=C); ^{1}H NMR (CCl_4) δ=1.26 (3H, t, *J*=7.2 Hz, CH_3), 3.66 (6H, s, 2×OCH_3), 4.16 (2H, q, *J*=7.2 Hz, OCH_2-), 6.5—7.3 (8H, m, ar. H), and 8.46 (1H, s, =CH-). Found: *m/z* 368.1258. Calcd for $C_{21}H_{20}O_6$: M, 368.1260.

3,3,8,8-Tetrakis(4-methoxyphenyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (12b): Amorphous solid.[2]

Decarboxylation of 2a, b, g. 2-Carboxy-2-methyl-4-butanolide (**2a, b, g**) (1 mmol) was heated in AcOH (30 cm^3) under reflux. After adding water (100 cm^3), the mixture was extracted with benzene and the solvent was evaporated in vacuo. The resulting crude product was purified on TLC with chloroform as the developing solvent, and in the case of **3g** further purification was made by TLC with ether/light petroleum 30 : 70 as the developing solvent.

2-Methyl-4,4-diphenyl-4-butanolide (3a): Heated for 9 h; 90% yield.

2-Methyl-4,4-bis(4-methoxyphenyl)-4-butanolide (3b): Heated for 6 h; 54% yield: Colorless prisms (from benzene/hexane); mp 100.1—100.4 °C; IR 1765 cm^{-1} (-COO-); ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, d, *J*=6.0 Hz, CH_3), 2.1—3.3 (3H, m, H-2 and 2×H-3), 3.74 (6H, s, 2×OCH_3), and 6.6—7.5 (8H, m, ar. H). Found: C, 73.16; H, 6.47%. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%.

2-Methyl-4-phenyl-4-butanolide (3g) (a mixture of two diasteroisomers, **3g′** and **3g″**): Heated for 5.5 h; 71% yield. **3g′**: From the upper fraction on TLC; liquid.[18] **3g″**: From the lower fraction on TLC; liquid.[18]

Dehydrobromination of 6a in AcOH. The **6a** (53.2 mg) was heated in AcOH (5 cm^3) at 100 °C for 1 h. The solvent was removed in vacuo and the resulting crude product was purified on TLC with chloroform as the developing solvent, giving 4,4-diphenyl-2-buten-4-olide (**8a**) (37.9 mg, 95%), mp 131.7—132.7 °C (lit,[19] mp 131—131.5 °C).

Reaction of 13 with 1a in the Presence of Manganese(III) Acetate. To a heated solution of **1a** (211.5 mg) and **13** (128 mg) in AcOH (20 cm^3), manganese(III) acetate (347.2 mg) was added. The solution was heated under reflux for 55 min. After adding water (100 cm^3), the mixture was extracted with benzene. After removal of the solvent in vacuo the resulting crude product was separated on TLC with benzene as the developing solvent, giving **11** (79%) and **12a** (5%).

Reaction of 13 with Manganese(III) Acetate. To a heated solution of **13** (204.5 mg) in AcOH (20 cm^3), manganese(III) acetate (353.4 mg) was added. The solution was heated under reflux for 90 min. After adding water (100 cm^3), the mixture was extracted with benzene and purified on TLC with benzene as the developing solvent, giving **10a** (24%) and **4** (6%).

Reaction of Phenylacetylene with Methylmalonic Acid in the Presence of Manganese(III) Acetate. To a heated solution of phenylacetylene (204.6 mg) and methylmalonic acid (284.1 mg) in AcOH (30 cm^3), manganese(III) acetate (1.289 g) was added. The solution was heated at 100 °C for 2 min. After adding water (100 cm^3), the mixture was extracted with benzene. The solvent was removed in vacuo and then the resulting crude product was purified on TLC with benzene as the developing solvent, giving **15′**, **15″**, and **16**.

2,2′-Dimethyl-4,4′-diphenyl-4,4′-bi(2-buten-4-olide) (15′): 18% yield: Colorless needles (from benzene); mp 229.7—230.5 °C; IR 1762 (-COO-) and 1659 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.59 (6H, d, *J*=1.3 Hz, 2×CH_3), 7.31 (10H, s, 2×Ph), and 7.41 (2H, q, *J*=1.3 Hz, H-3 and H-3′). Found: C, 76.27; H, 5.23%. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24%.

Stereoisomeric 2,2′-Dimethoxy-4,4′-diphenyl-4,4′-bi(2-buten-4-olide) (15″): 7% yield: Colorless microcrystals (**15″** has changed to **15′** during recrystallization from benzene); IR

1763 (-COO-) and 1658 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ=1.91 (6H, d, J=1.3 Hz, 2×CH$_3$), 7.15 (10H, s, 2×Ph), 7.33 (2H, q, J=1.3 Hz, H-3 and H-3').

4-Acetoxy-2-methyl-4-phenyl-2-buten-4-olide (16): Liquid; IR 1783 (-COO-), 1748 (OAc), and 1664 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ=1.95 (3H, d, J=1.3 Hz, CH$_3$), 2.04 (3H, s, OAc), 7.1—7.6 (5H, m, Ph), and 7.30 (1H, q, J=1.3 Hz, =CH-). Found: m/z 232.0731. Calcd for $C_{13}H_{12}O_4$: M, 232.0736.

We wish to thank Professor Hitoshi Takeshita and Associate Professor Akira Mori of the Research Institute of Industrial Science, Kyushu University, and Dr. Shinzaburo Hishida of Hitachi Ltd., for their measurements of the mass spectra.

References

1) J. B. Bush, Jr. and H. L. Finkbeiner, *J. Am. Chem. Soc.*, **90**, 5903 (1968); E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 5905 (1968).

2) N. Ito, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **56**, 3527 (1983).

3) W. E. Fristad and S. S. Hershberger, *J. Org. Chem.*, **50**, 1026 (1985).

4) Although an oxo-centered trinuclear structure for manganese(III) acetate in solid state was proposed (Ref. 5), we have calculated the molar equivalent for the acetate as Mn(OAc)$_3$·2H$_2$O according to Dewar et al. (P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966)).

5) W. E. Fristad and J. R. Peterson, *J. Org. Chem.*, **50**, 10 (1985).

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

7) E. J. Corey and A. W. Gross, *Tetrahedron Lett.*, **26**, 4291 (1985).

8) M. Okano, *Chem. Lett.*, **1973**, 165.

9) W. E. Fristad, J. R. Peterson, and A. B. Ernst, *J. Org. Chem.*, **50**, 3143 (1985).

10) T. Nakano, K. Ohkawa, S. Ikemori, H. Matsumoto, and Y. Nagai, *Nippon Kagaku Kaishi*, **1983**, 1778.

11) R. Anshütz and A. Hilbert, *Ber.*, **57**, 1697 (1924).

12) C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **49**, 546 (1927).

13) M. Conrad and H. Reibach, *Ber.*, **35**, 1813 (1902).

14) W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

15) D. F. Bender, T. Thippeswamy, and W. L. Rellahan, *J. Org. Chem.*, **35**, 939 (1970).

16) T. Nakano, K. Ohkawa, S. Ikemori, R. Hasegawa, Y. Sako, H. Matsumoto, and Y. Nagai, *Nippon Kagaku Kaishi*, **1983**, 1770.

17) V. K. Kasal and A. P. Bhaduri, *Z. Naturforsh.*, **34B**, 1567 (1979); *Chem. Abstr*, **92**, 110502x (1980).

18) A. P. Kozikowski and Y.-Y. Chen, *J. Org. Chem.*, **45**, 2236 (1980).

19) P. M. M. van Haard, L. Thijs, and B. Zwanenburg, *Tetrahedron Lett.*, **1975**, 803.