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

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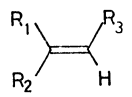
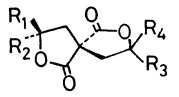
Synopsis. The reaction of 1,1-diphenylethene with malonic acid in the presence of manganese(III) acetate gave 3,3,8,8-tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione and 4,4-diphenyl-2-(2,2-diphenylethenyl)-4-butanolide. Similar reactions with 1,1-bis(4-methoxyphenyl)ethene, methylenecyclohexane, 2-phenylpropene, 1-octene, and cyclohexene yielded the corresponding 2,7-dioxaspiro[4.4]nonane-1,6-diones.

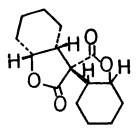
The formation of γ-lactone in the reaction of olefins with manganese(III) acetate (MA) in acetic acid (AcOH) has been reported.[1] Similar α-substituted γ-lactone formations have been observed when the reaction was carried out in the presence of propionic acid,[2] cyanoacetic acid, isobutyric acid, and succinic acid.[1] These results led us to examine the reaction of olefins with malonic acid in the presence of MA. When a mixture of 1,1-diphenylethene (**1a**) and malonic acid was oxidized with MA in AcOH, 3,3,8,8-tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2a**), 4,4-diphenyl-2-(2,2-diphenylethenyl)-4-butanolide (**3**), and benzophenone (**4**) were obtained. 1,1-Bis(4-methoxyphenyl)ethene (**1b**) and methylenecyclohexane (**1c**) gave the corresponding 2,7-dioxaspiro[4.4]nonane-1,6-diones (**2b** and **2c**). The reactions of 2-phenylpropene (**1d**), styrene (**1e**), and 1-octene (**1f**) yielded three isomeric 2,7-dioxaspiro[4.4]nonane-1,6-diones, (**2d'**, **2d''**, **2d'''**), (**2e'**, **2e''**, **2e'''**), and (**2f'**, **2f''**, **2f'''**). Their configurations could be determined on the basis of ^{1}H-NMR spectral analyses. The reaction of cyclohexene (**1g**) with malonic acid in the presence of MA gave cyclohexenyl acetate (**5**) and a mixture of dodecahydro-3,3'(2*H*,2'*H*)-spirobi[benzofuran]-2,2'-diones (**2g'**, **2g''**, and **2g'''**)(27%). In contrast to disubstituted olefins, the reaction of 1,1,2-triphenylethene (**1h**) with malonic acid in the presence of MA gave 1,1,2-triphenyl-1,2-ethanediol 2-acetate (**6**) and 3,4,4-triphenyl-4-butanolide (**7**).



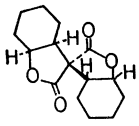


1a $R_1=R_2=Ph$, $R_3=H$
1b $R_1=R_2=C_6H_4OCH_3$, $R_3=H$
1c $R_1=R_2=-(CH_2)_5-$, $R_3=H$
1d $R_1=Ph$, $R_2=CH_3$, $R_3=H$
1e $R_1=Ph$, $R_2=R_3=H$
1f $R_1=$hexyl, $R_2=R_3=H$
1g $R_1=R_3=-(CH_2)_4-$, $R_2=H$

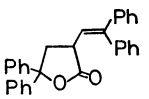
2a $R_1=R_2=R_3=R_4=Ph$
2b $R_1=R_2=R_3=R_4=C_6H_4OCH_3$
2c $R_1=R_2=-(CH_2)_5-$, $R_3=R_4=-(CH_2)_5-$
2d' $R_1=R_4=Ph$, $R_2=R_3=CH_3$
2d'' $R_2=R_3=Ph$, $R_1=R_4=CH_3$
2d''' $R_1=R_3=Ph$, $R_2=R_4=CH_3$
2e' $R_1=R_4=Ph$, $R_2=R_3=H$
2e'' $R_2=R_3=Ph$, $R_1=R_4=H$
2e''' $R_1=R_3=Ph$, $R_2=R_4=H$
2f' $R_1=R_4=$hexyl, $R_2=R_3=H$
2f'' $R_2=R_3=$hexyl, $R_1=R_4=H$
2f''' $R_1=R_3=$hexyl, $R_2=R_4=H$



2g'



2g''



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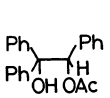

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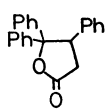

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Experimental

Reaction of Olefins with Malonic Acid in the Presence of MA. To a heated solution of olefin (2 mmol) and malonic acid (1 mmol) in AcOH (20 ml), MA[6] (4 mmol) was added. The solution was heated under reflux for 1—5 min. After water (100 ml) being added, the mixture was extracted with chloroform or dichloromethane. The solvent was removed *in vacuo* and the resulting crude product was separated on TLC with chloroform or benzene as the developing solvent, and in the cases of **2f** and **2g** further separation was made by HPLC, eluting with aqueous methanol.

Oxidation Products from 1,1-Diphenylethene[7] *(**1a**). 3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2a**)*: Colorless needles: mp 284.5—285.0 °C (from benzene); 84% yield; IR ($CHCl_3$) 1770 (C=O) and 1793 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.62 (2H, d, J=13.5 Hz, 2×-HCH-), 3.03 (2H, d, J=13.5 Hz, 2×-HCH-), 7.24 (10H, s, 2×Ph), and 7.35 (10H, s, 2×Ph). Found: C, 80.87; H, 5.47%. Calcd for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25%.

*4,4-Diphenyl-2-(2,2-diphenylethenyl)-4-butanolide (**3**)*: Colorless prisms; mp 165—166 °C (methanol); 5% yield; IR ($CHCl_3$) 1772 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.66 (1H, dd, J=12.7 and 11.4 Hz, -HCH-), 3.12 (1H, dd, J=7.8 and 12.7 Hz, -HCH-), 3.51 (1H, m, -CH<), 6.62 (1H, d, J=8.8 Hz, =CH-), and 7.01—7.41 (20H, m, 4×Ph). Found: m/z 416.17511. Calcd for $C_{30}H_{24}O_2$: M, 416.17763.

*Benzophenone (**4**)*: Colorless plates; mp 47—48 °C (methanol); 1%.

Oxidation Product of 1,1-Bis(4-methoxyphenyl)ethene[8] *(**1b**). 3,3,8,8-Tetrakis(4-methoxyphenyl)-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2b**)*: Amorphous solid (methanol); 84% yield; IR ($CHCl_3$) 1768 (C=O) and 1790 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.54 (2H, d, J=13.0 Hz, 2×-HCH-), 2.94 (2H, d, J=13.0 Hz, 2×-HCH-), 3.72 (6H, s, 2×OCH_3), 3.80 (6H, s, 2×OCH_3), and 6.65—7.30 (16H, m, aromatic). Found: m/z 580.20720. Calcd for $C_{35}H_{32}O_8$: M, 580.20972.

Oxidation Product of Methylenecyclohexane[9] *(**1c**). 16,19-Dioxatrispiro[5.1.1.5.2.2]nonadecane-17,18-dione (**2c**)*: Colorless plates; mp 165—166 °C (methanol); 27% yield; IR ($CHCl_3$) 1758 (C=O) and 1774 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.0—2.4 (20H, 2×-$(CH_2)_5$-), 2.11 (2H, d, J=13 Hz, 2×-HCH-), 2.63 (2H, d, J=13 Hz, 2×-HCH-). Found: m/z 292.17128. Calcd for $C_{17}H_{24}O_4$: M, 292.16746.

Oxidation Products from 2-Phenylpropene[10] (**1d**). (3R*, 5R*,8R*)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2d'**): Colorless needles; mp 162—163 °C (methanol); 10% yield; IR ($CHCl_3$) 1768 (C=O) and 1785 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.75 (6H, s, 2×CH_3), 2.17 (2H, d, J=13.4 Hz, 2×-HCH-), 2.68 (2H, d, J=13.4 Hz, 2×-HCH-), 7.14—7.43 (10H, m, 2×Ph); HPLC R_t (retention time)(eluent) 12.6 min (70% aqueous methanol). Found: m/z 336.12992. Calcd for $C_{21}H_{20}O_4$: M, 336.13600.

(3S*,5R*,8S*)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]-nonane-1,6-dione (**2d''**): Colorless needles; mp 218—219 °C (methanol); 19% yield; IR ($CHCl_3$) 1768 (C=O) and 1789 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.77 (6H, s, 2×CH_3), 2.72 (2H, d, J=13.4 Hz, 2×-HCH-), 3.24 (2H, d, J=13.4 Hz, 2×-HCH-), and 7.34—7.45 (10H, m, 2×Ph); HPLC R_t 8.3 min (70% aqueous methanol). Found: m/z 336.13550. Calcd for $C_{21}H_{20}O_4$: M, 336.13600.

(3R*,5R*,8S*)-3,8-Dimethyl-3,8-diphenyl-2,7-dioxaspiro[4.4]-nonane-1,6-dione (**2d'''**): Colorless plates; mp 98.5—99.5 °C (methanol); 39% yield; IR ($CHCl_3$) 1768 (C=O) and 1785 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.66 (3H, s, CH_3), 1.86 (3H, s, CH_3), 2.08 (1H, d, J=13.2 Hz, -HCH-), 2.79 (1H, d, J=13.5 Hz, -HCH-), 2.83 (1H, d, J=13.2 Hz, -HCH-), 3.20 (1H, d, J=13.5 Hz, -HCH-), 7.32 (5H, m, Ph), and 7.37 (5H, m, Ph); HPLC R_t 10.5 min (70% aqueous methanol). Found: C, 75.19; H, 6.02%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

Oxidation Products from Styrene (**1e**). (3R*,5R*,8R*)-3,8-Diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2e'**): Colorless plates; mp 162—163 °C (methanol); 9% yield; IR ($CHCl_3$) 1770 (C=O) and 1788 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.23 (2H, dd, J=13.5 and 9.0 Hz, 2×-HCH-), 3.09 (2H, dd, J=13.5 and 6.5 Hz, 2×-HCH-), 5.93 (2H, dd, J=9.0 and 6.5 Hz, 2×-CH<), and 7.33 (10H, s, 2×Ph); HPLC R_t 9.2 min (70% aqueous methanol). Found: m/z 308.10706. Calcd for $C_{19}H_{16}O_4$: M, 308.10486.

(3S*,5R*,8S*)-3,8-Diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2e''**): Colorless needles; mp 236—237 °C ($CHCl_3$); 30% yield; IR ($CHCl_3$) 1762 (C=O) and 1782 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.87 (2H, m, 2×-HCH-), 2.79 (2H, m, 2×-HCH-), 5.50 (2H, t, J=8.0 Hz, 2×-CH<), and 7.50 (10H, s, 2×Ph); HPLC R_t 6.3 min (70% aqueous methanol). Found: m/z 308.10564. Calcd for $C_{19}H_{16}O_4$: M, 308.10486.

(3R*,5R*,8S*)-3,8-Diphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2e'''**): Colorless needles; mp 185—186 °C (benzene); 40% yield; IR ($CHCl_3$) 1768 (C=O) and 1786 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.15—3.37 (4H, m, 2×-CH_2-), 5.56 (1H, dd, J=10 and 7 Hz, -CH<), 5.86 (1H, dd, J=10 and 6 Hz, -CH<), 7.40 (5H, s, Ph), and 7.42 (5H, s, Ph); HPLC R_t 7.4 min (70% aqueous methanol). Found: C, 74.01; H, 5.23%. Calcd for $C_{19}H_{16}O_2$: C, 74.00; H, 4.99%.

Oxidation Products from 1-Octene (**1f**). (3S*,5R*,8S*)-3,8-Dihexyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2f'**): Colorless needless; mp 116.5—118.0 °C (methanol); 4% yield; IR ($CHCl_3$) 1762 (C=O) and 1780 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=0.6—2.1 (26H, m, 2×-C_6H_{13}), 1.88 (2H, dd, J=13 and 9 Hz, 2×-HCH-), 2.75 (2H, dd, J=13 and 6 Hz, 2×-HCH-), 4.5—5.1 (2H, m, 2×-CH<); HPLC R_t 10.0 min (80% aqueous methanol). Found: m/z 324.23226. Calcd for $C_{19}H_{32}O_4$: M, 324.23006.

(3R*,5R*,8R*)-3,8-Dihexyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2f''**): Colorless needles; mp 112.5—113.5 °C (methanol); 17% yield; IR ($CHCl_3$) 1762 (C=O) and 1782 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=0.7—2.1 (26H, m, 2×-C_6H_{13}), 2.41 (4H, d, J=8 Hz, 2×-CH_2-), and 4.42 (2H, br. q, J=8 Hz, 2×-CH<); HPLC R_t 6.6 min (80% aqueous methanol). Found: C, 75.53; H, 10.00%. Calcd for $C_{19}H_{32}O_4$: C, 75.34; H, 9.94%.

(3S*,5R*,8R*)-3,8-Dihexyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**2f'''**): Colorless needles; mp 110—111 °C (methanol); 19% yield; IR ($CHCl_3$) 1762 (C=O) and 1778 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=0.7—2.1 (26H, m, 2×-C_6H_{13}), 1.70—2.95 (4H, m, 2×-CH_2-), and 4.2—5.1 (2H, m, 2×-CH<); HPLC R_t 7.8 min (80% aqueous methanol). Found: m/z 324.23135. Calcd for $C_{19}H_{32}O_4$: M, 324.23006.

Oxidation Products from Cyclohexene (**1g**). (3R*,3aR*,3'aR*,7aR*,7'aR*)-Dodecahydro-3,3'(2H,2'H)-spirobi[benzofuran]-2,2'-dione (**2g'**): Colorless needles; mp 285—286 °C (methanol); IR ($CHCl_3$) 1766 (C=O) and 1792 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.10—1.85 (14H, m, 6×-CH_2- and 2×-CH<), 2.29 (2H, br. d, J=13.9 Hz, 2×-CH<), 2.50 (2H, m, $w_{1/2}$=22 Hz, 2×-HCH-), and 4.62 (2H, m, $w_{1/2}$=9 Hz, -OCH<); HPLC R_t 5.6 min (70% aqueous methanol). Found: m/z 264.13606. Calcd for $C_{15}H_{20}O_4$: M, 264.13616.

(3R*,3aS*,3'aR*,7aS*,7'aR*)-Dodecahydro-3,3'(2H,2'H)-spirobi[benzofuran]-2,2'-dione (**2g''**): Colorless needles; mp 190—191 °C (methanol); IR ($CHCl_3$) 1766 (C=O) and 1792 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.0—1.8 (13H, m, 6×-CH_2- and -HCH-), 2.20—2.35 (3H, m, 3×-HCH-), 2.50 (2H, m, $w_{1/2}$=24 Hz, 2×-CH<), 4.51 (1H, m, $w_{1/2}$=8 Hz, -OCH<), and 4.84 (1H, m, $w_{1/2}$=8 Hz, -OCH<); HPLC R_t 7.0 min (70% aqueous methanol). Found: m/z 264.13647. Calcd for $C_{15}H_{20}O_4$: M, 264.13616.

Dodecahydro-3,3'-(2H,2'H)-spirobi[benzofuran]-2,2'-dione (**2g'''**) (configuration is unknown): Colorless needles; mp 186—187 °C (methanol); IR ($CHCl_3$) 1770 (C=O) and 1792 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=1.1—2.0 (14H, m, 7×-CH_2-), 2.2—2.5 (3H, m, 2×-HCH- and -CH<), 2.67 (1H, m, $w_{1/2}$=24 Hz, -CH<), 3.99 (1H, m, $w_{1/2}$=27 Hz, -OCH<), and 4.50 (1H, m, $w_{1/2}$=13 Hz, -OCH<); HPLC R_t 6.0 min (70% aqueous methanol). Found: m/z 264.13625. Calcd for $C_{15}H_{20}O_4$: M, 264.13616.

Cyclohexenyl Acetate (**5**): Colorless liquid; 22% yield.

Oxidation Products from 1,1,2-Triphenylethene[11] (**1h**). 1,1,2-Triphenyl-1,2-ethanediol 2-Acetate (**6**): Colorless needles; mp 224.5—225.5 °C (benzene) (lit,[12] mp 217—219 °C); 22% yield; IR ($CHCl_3$) 1736 (OAc) and 3592 cm^{-1} (OH); ^{1}H-NMR ($CDCl_3$) δ=1.93 (3H, s, OAc), 2.27 (1H, s, OH), 6.68 (1H, s, -CH<), and 7.1—7.7 (15H, m, 3×Ph).

3,4,4-Triphenyl-4-butanolide (**7**): Pale yellow needles; mp 96.0—96.5 °C (methanol); 3% yield; IR ($CHCl_3$) 1776 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.75 (1H, dd, J=17 and 5 Hz, -HCH-), 2.93 (1H, dd, J=17 and 7 Hz, -HCH-), 4.46 (1H, dd, J=7 and 5 Hz, -CH<). Found: m/z 314.13397. Calcd for $C_{22}H_{18}O_2$: M, 314.13068.

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