  Bull. Chem. Soc. Jpn., 54, 2391—2394 (1981)

The Oxidation of 3,3-Diphenyl-2-propenoic Acid with Manganese(III) Acetate

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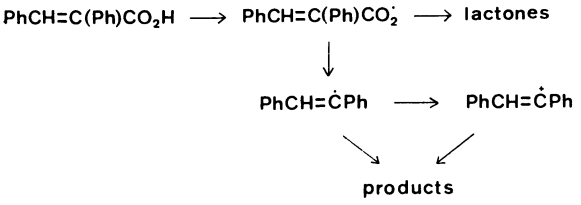
(Received November 8, 1980)

The oxidation of 3,3-diphenyl-2-propenoic acid with manganese(III) acetate in boiling acetic acid gave 3,3-diphenyl-2-propenyl acetate, 4-acetoxymethyl-5,5-diphenyltetrahydro-2-furanone, 3,3-diphenyl-2-propenal, 5,5-diphenyl-2,5-dihydro-2-furanone, 4-acetoxy-5,5-diphenyltetrahydro-2-furanone, benzophenone, and 2-oxo-5,5-diphenyltetrahydro-4-furancarboxylic acid. The reaction pathways are discussed.

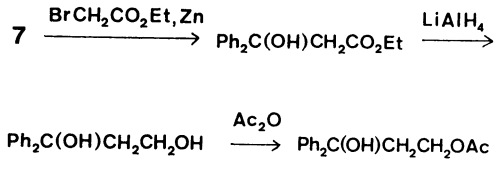
In a previous report[1] we described the oxidation of (*E*)-2,3-diphenyl-2-propenoic acids with manganese(III) acetate. The results were explained in terms of the formation of an acyloxy radical, a vinyl radical, and a vinyl cation from (*E*)-2,3-diphenyl-2-propenoic acid and the subsequent reactions of these intermediates (Scheme 1). We have now examined the oxidation of 3,3-diphenyl-2-propenoic acid (**1**) with manganese(III) acetate; the results will be described in this paper.



Scheme 1.

When 3,3-diphenyl-2-propenoic acid (**1**) was oxidized with manganese(III) acetate in the molar ratios of 1 : 3, 1 : 4, and 1 : 6 in boiling acetic acid, 3,3-diphenyl-2-propenyl acetate (**2**), 4-acetoxymethyl-5,5-diphenyltetrahydro-2-furanone (**3**), 3,3-diphenyl-2-propenal (**4**), 4-acetoxy-5,5-diphenyltetrahydro-2-furanone (**5**), 5,5-diphenyl-2,5-dihydro-2-furanone (**6**), and benzophenone (**7**) were obtained. When the oxidation was conducted in acetic acid containing acetic anhydride, 2-oxo-5,5-diphenyltetrahydro-4-furancarboxylic acid (**8**) was obtained, along with other products (**2**—**4**, and **6**), but **5** and **7** were not obtained. The results are summarized in Table 1. The structures of the products were determined by means of a study of their IR, NMR, and MS spectra, by elemental analyses, and by comparison with authentic samples.

3,3-Diphenyl-2-propenyl acetate (**2**) was obtained in the oxidation; the yield first increased with the increase in the molar ratio of the oxidant to the substrate, and then it decreased, suggesting that **2** could be further oxidized. In fact, the oxidation of **2**, prepared separately (Scheme 2), with manganese(III) acetate gave Compounds **3**, **4**, and **7** (Entry 8), **3** being the main product. The fact that only a small amount of **7** was formed from **2** indicates that **7** in Entries 1, 3, and 5 was not mainly formed *via* **2**. It seemed that the reaction of **1** with manganese(III) acetate would give an acyloxy radical (**A**), which then decomposed to a 2,2-diphenylethenyl radical (**B**), and that the latter reacted with the carboxymethyl radical formed from manganese(III) acetate to give 4,4-diphenyl-3-butenoic acid (**9**) (Scheme

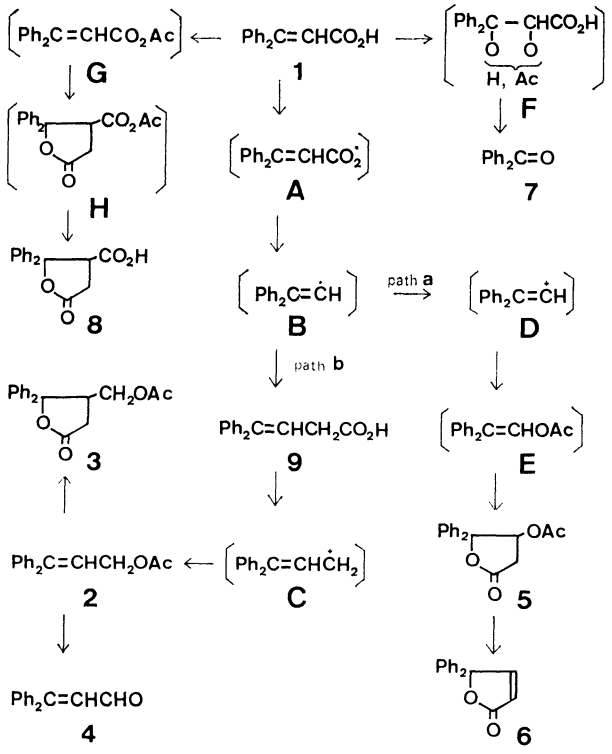


Scheme 2.

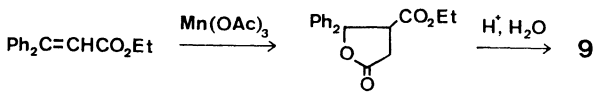
TABLE 1. THE REACTION OF 3,3-DIPHENYL-2-PROPENOIC ACID (**1**) AND RELATED COMPOUNDS WITH MANGANESE(III) ACETATE IN BOILING ACETIC ACID CONTAINING ACETIC ANHYDRIDE

Entry	Substrate	Molar ratio of substrate : oxidant : Ac_2O	Time / min	Recovered substrate / %	Yield/%[a]							
					2	**3**	**4**	**5**	**6**	**7**	**8**	**11**
1	**1**	1 : 3 : 0	240	30	13	3	4	<1	1	19		
2	**1**	1 : 3 : 50	10	26	9	21	2		<1		8	
3	**1**	1 : 4 : 0	360	17	18	22	<1	<1	2	18		
4	**1**	1 : 4 : 50	13	2	4	35	2		<1		9	
5	**1**	1 : 6 : 0	420	9	14	36	4		3	18		
6	**1**	1 : 6 : 50	20			45					10	
7	**1**[b]	1 : 2 : 50	30	13	7	7					19	
8	**2**	1 : 2 : 0	600	17		58	4			4		
9	**2**	1 : 2 : 50	10	9		89						
10	**8**	1 : 2 : 0	150	32	30	25						
11	**9**	1 : 2 : 0	30		48		<1			<1		
12	**10**	1 : 3 : 6	60	9	4					9		71

a) The yields are based on the amount of the substrate used. b) **1** was pre-treated with excess acetyl chloride before the reaction.



Scheme 3.

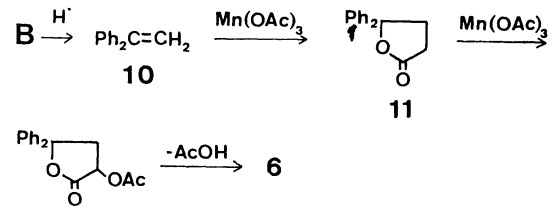


Scheme 4.

3, Path b). However, **9** could not be found in the products. Therefore, **9** was synthesized separately (Scheme 4) and treated with manganese(III) acetate. As a result, **2** was obtained as a single product (Entry 11), showing that **9** is a possible precursor of **2**.

4-Acetoxymethyl-5,5-diphenyltetrahydro-2-furanone (**3**) was obtained as the main product in the oxidation of **1** with manganese(III) acetate in Entries 2—6; the yield increased much with the increase in the oxidant. The oxidation of **2** with manganese(III) acetate in acetic acid containing acetic anhydride gave **3** almost exclusively (Entry 9).

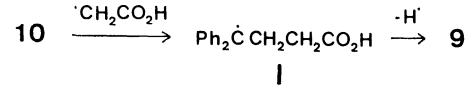
Benzophenone (**7**) was obtained in a fairly large quantity, although it could not be separated from **2** because they have the same R_f values on TLC. However, on HLC it clearly showed two peaks corresponding to those of authentic samples. It is also interesting to note that benzophenone (**7**) was not formed in the reactions of **1** and **2** when acetic anhydride was added. It is known that the yield of lactones increases in the reaction of olefins with mangenese(III) acetate with a lowering of the water content in the reaction mixture.[2] It seems possible to assume that there are pathways which afford a hydroxy acetate like **F** and then **7** in the oxidation of **1** and **2**, and that these pathways do not operate under anhydrous conditions. It has been reported that the cleavage of the double



Scheme 5.

bond of chalcones in the oxidation with manganese(III) acetate gave a benzaldehyde,[3] although the reaction pathway was not shown.

As another interesting feature of the reaction, it gave 5,5-diphenyl-2,5-dihydro-2-furanone (**6**) in very low yields (Entries 1, 3, and 5). We oxidized **2**, **8**, and **9**, but none of them gave the lactone (**6**). It seemed possible that acetoxylation of 5,5-diphenyltetrahydro-2-furanone (**11**), followed by decomposition, might give the lactone (**6**), as is shown in Scheme 5. The oxidation of 1,1-diphenylethylene (**10**) with manganese(III) acetate gave **11** as the major product, together with **2** and **7** in minor quantitities (Entry 12), but it did not give **6**. The formation of **2** from **10** can be explained as follows. The addition of a carboxymethyl radical to **10** gives a radical, **I**, which then loses a hydrogen radical to yield **9** and then **2** (Scheme 6). One of the minor



Scheme 6.

fractions isolated from the reaction of **1** with manganese(III) acetate in acetic acid showed a peak at $\delta=1.69$ corresponding to an acetoxyl group. The purification of the fraction by repeated TLC failed to give a pure compound, but the NMR spectrum showed three aliphatic protons, at $\delta=2.45$ (1H, dd, $J=2.5$ and 18.0 Hz), $\delta=2.72$ (1H, $J=6.0$ and 18.0 Hz), and $\delta=6.25$ (1H, dd, $J=2.5$ and 6.0 Hz). Since the chemical shift ($\delta=1.69$) for the acetoxyl group is higher than the normal one ($\delta=2$), and since the J value of 18.0 Hz for methylene protons adjacent to a carbonyl function is comparable to those of cyclic compounds, the structure of this compound must be 4-acetoxy-5,5-diphenyltetrahydro-2-furanone (**5**). When the fraction was heated in acetic acid under reflux, it gave **6**. Thus, it is most probable that **6** was formed from **5**.

3,3-Diphenyl-2-propenal (**4**) was obtained as a minor product which might have been formed from **2** by further oxidation with manganese(III) acetate and hydrolysis during the work-up.

The formation of 2-oxo-5,5-diphenyltetrahydro-4-furancarboxylic acid (**8**) in the reaction containing acetic anhydride seems to indicate that **1** forms an anhydride with acetic anhydride and then reacts with the carboxymethyl radical. The reaction of **1** which had been pretreated with acetyl chloride gave **8** in a much improved yield (Entry 7). Since the reaction of **8** with manganese(III) acetate gave **2** and **3** (Entry 10), therefore, it seems that **8** could be decarboxylated to give **9** which

yielded **2** and **3**. However, **8** cannot be a real precursor for **2** and the other compounds in the oxidation of **1**, because if **8** were first formed and then oxidized to **2**, **3**, and **4** during the prolonged reaction time in the reaction in acetic acid, the total yield of **2**, **3**, **4**, and **8** should be roughly equal to that in the reaction in acetic acid containing acetic anhydride. However, this was not the case. For example, the total yield (20%) of **2**, **3**, **4**, and **8** in Entry 1 was less than that (40%) in Entry 2. The above possible reaction pathways are summarized in Scheme 3.

Experimental

All the 60 MHz ^1H NMR spectra were recorded with a Hitachi R-24 spectrometer, while the 100 MHz ^1H NMR spectrum was taken on a JEOL MH-100 spectrometer, with TMS as the internal standard. The IR spectra were recorded for the chloroform solution with a JASCO IRA-1 grating spectrometer, while the MS spectra were taken with JMS-01 SG-2 and Hitachi M-80 plus M-003 instruments. Liquid chromatography (HLC) was carried out with a Mitsubishi ALTEX 310/330 instrument, eluting with 60% aqueous methanol using a HY-ODS-SU column 4.6 mm in diameter and 250 mm in length. The melting points were determined on a Yanagimoto micro-melting point apparatus and were not corrected.

Materials. The 3,3-Diphenyl-2-propenoic acid (**1**) was prepared by the standard procedure[4] from benzophenone. The ethyl 3,3-diphenyl-2-propenoate[5] was prepared by the dehydration of ethyl 3-hydroxy-3,3-diphenylpropanoate[4] with thionyl chloride in pyridine.

3-Acetoxy-1,1-diphenyl-1-propanol. To ethyl 3-hydroxy-3,3-diphenylpropanoate (1.95 g) in anhydrous diethyl ether (100 ml), we added lithium aluminium hydride (80 mg), after which the mixture was stirred at 0 °C for 14 h. After the addition of 1 M (1 M=1 mol dm^{-3}) sulfuric acid (50 ml), the reaction mixture was extracted with diethyl ether. The combined ethereal extract was washed with a saturated solution of sodium chloride and then evaporated. The resulting 1,1-diphenyl-1,3-propanediol was treated with a mixture of acetic anhydride (5 ml) and pyridine (10 ml) at room temperature for 17 h. The reaction mixture was poured into iced water, and the precipitate was collected and recrystallized from light petroleum to give 3-acetoxy-1,1-diphenyl-1-propanol (1.80 g, 92%), mp 84—85 °C; IR 1740 (OAc) and 3560 cm^{-1} (OH); NMR ($CDCl_3$) δ=1.88 (3H, s, OAc), 2.61 (2H, t, J=7.0 Hz, $-CH_2-$), 2.79 (1H, s, OH), 4.16 (2H, t, J=7.0 Hz, $-CH_2-$), and 7.1—7.6 (10H, m, 2×Ph). Found: C, 75.48; H, 6.49%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

3,3-Diphenyl-2-propenyl Acetate (2). A solution of 3-acetoxy-1,1-diphenyl-1-propanol (1.40 g) in pyridine (10 ml) was treated with thionyl chloride (1.24 g) at 0 °C for 19 h. The reaction mixture was poured into 1 M sulfuric acid (100 ml) and then extracted with benzene (50 ml). The benzene layer was washed with 1 M sulfuric acid (30 ml) and then evaporated, giving **2** (1.21 g, 86%). The analytical sample was distilled under reduced pressure; bp 150—155 °C (bath temp)/0.1 mmHg (1 mmHg=133.322 Pa); IR 1738 cm^{-1} (OAc); NMR (CCl_4) δ=1.97 (3H, s, OAc), 4.54 (2H, d, J=7.0 Hz, $-CH_2-$), 6.15 (1H, t, J=7.0 Hz, >CH–), and 7.2 (10H, m, 2×Ph); MS *m/e* 252.1187 (Calcd for $C_{17}H_{16}O_2$: 252.1150) (59%, M^+), 209 (61%), 192 (100%), and 103 (82%).

Ethyl 2-Oxo-5,5-diphenyltetrahydro-4-furancarboxylate. A mixture of ethyl 3,3-diphenyl-2-propenoate (504 mg), manganese(III) acetate dihydrate[6] (1.61 g), acetic acid (20 ml), and acetic anhydride (3 ml) was heated under reflux for 43 min. The reaction mixture was poured into water (50 ml), and the precipitate was collected. Recrystallization from ethanol gave ethyl 2-oxo-5,5-diphenyltetrahydro-4-carboxylate (513 mg, 90%); mp 147—148 °C; IR 1742 (COOEt) and 1780 cm^{-1} (lactone); NMR ($CDCl_3$) δ=0.92 (3H, t, J=7.0 Hz, $-CH_3$), 2.71 (1H, dd, J=8.5 and 18.0 Hz, –CH–), 3.02 (1H, dd, J=4.5 and 18.0 Hz, –CH–), 3.75 (2H, m, $-CH_2-$), 4.20 (1H, dd, J=8.5 and 4.5 Hz, –CH–), and 7.2—7.8 (10H, m, 2×Ph). Found: C, 73.40; H, 5.65%. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85.

4,4-Diphenyl-3-butenoic Acid (9). A mixture of ethyl 2-oxo-5,5-diphenyltetrahydro-4-furancarboxylate (572 mg), 3 M hydrochloric acid (100 ml), and ethanol (100 ml) was heated under reflux for 21 h. After the removal of the ethanol and the hydrochloric acid, the resulting mixture was extracted with benzene; then the benzene solution was extracted with a saturated sodium hydrogencarbonate solution. The aqueous solution was separated and acidified with concd hydrochloric acid. The precipitate was collected and recrystallized from a mixture of carbon tetrachloride–light petroleum to give 4,4-diphenyl-3-butenoic acid (115 mg, 25%); mp 109—111 °C; IR 1725 (COOH) and 2400—3400 cm^{-1} (COOH); NMR ($(CD_3)_2SO$) δ=3.06 (2H, d, J=8.0 Hz, $-CH_2-$), 6.26 (1H, t, J=8.0 Hz, =CH–), and 7.3 (10H, m, 2×Ph); MS *m/e* 238.1008 (Calcd for $C_{16}H_{14}O_2$: 238.0994) (66%, M^+), 193 (85%), 178 (53%), and 115 (100%).

Oxidations of 3,3-Diphenyl-2-propenoic Acid (1), 3,3-Diphenyl-2-propenyl Acetate (2), 2-Oxo-5,5-diphenyltetrahydro-4-furancarboxylic Acid (8), 4,4-Diphenyl-3-butenoic Acid (9), and 1,1-Diphenylethylene (10). The general procedure for the oxidation of 3,3-diphenyl-2-propenoic acid (**1**) and the other compounds (**2**, **8**, **9**, and **10**) was as follows. A mixture of the substrate (2 mmol), manganese(III) acetate dihydrate (4—12 mmol), acetic acid (30 ml), and acetic anhydride (when it was needed) (10 ml) was heated under reflux until the dark color of Mn(III) ion disappeared (the time is shown in Table 1). After the removal of the acetic acid, 1 M sulfuric acid (30 ml) was added to the mixture, which was then extracted with benzene (30 ml). The benzene solution was washed with aqueous sodium hydrogencarbonate and evaporated under reduced pressure. The products were separated on TLC (Wakogel B 10), with chloroform as the developing solvent, and then recrystallized. The aqueous sodium hydrogencarbonate solution was acidified with concd hydrochloric acid and extracted with chloroform, which gave acidic products. The yields are summarized in Table 1.

Oxidation Products. *3,3-Diphenyl-2-propenyl Acetate (2)*: Liquid (this was identical with an authentic sample).

4-Acetoxymethyl-5,5-diphenyltetrahydro-2-furanone (3): Mp 119—120 °C (EtOH); IR 1752 (OAc) and 1780 cm^{-1} (lactone); NMR (C_6H_6) δ (100 MHz)=1.60 (3H, s, OAc), 2.12 (2H, d, J=6.0 Hz, $-CH_2-$), 3.16 (1H, m, –CH–), 3.40 (1H, dd, J=8.0 and 11.5 Hz, –CH–), and 3.94 (1H, dd, J=4.5 and 11.5 Hz, –CH–). Found: C, 73.39; H, 5.97%. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85%.

3,3-Diphenyl-2-propenal (4): Liquid (lit,[7] mp 44 °C); IR 1680 cm^{-1} (CHO); NMR ($CDCl_3$) δ=6.56 (1H, d, J=9.0 Hz, =CH–) 7.35 (10H, m, 2×Ph), and 9.49 (1H, d, J=9.0 Hz, CHO); MS *m/e* 208.0896 (Calcd for $C_{15}H_{12}O$: 208.0888) (100%, M^+), 207 (99%), 178 (39%), 165 (22%), 152 (14%), 131 (19%), and 102 (38%).

4-Acetoxy-5,5-diphenyltetrahydro-2-furanone (5): Liquid (this compound was obtained as a mixture; its NMR data are given in the text).

5,5-Diphenyl-2,5-dihydro-2-furanone (6): Mp 128—128.5 °C

(EtOH) (lit,[8] mp 131—131.5 °C); IR 1680 (C=C) and 1770 cm^{-1} (lactone); NMR ($CDCl_3$) δ=6.11 (1H, d, J=6.0 Hz, =CH–), 7.26 (10H, m, 2×Ph), and 7.87 (1H, d, J=6.0 Hz, =CH–); MS *m/e* 236 (41%, M^+), 131 (100%), 105 (83%), and 77 (69%).

Benzophenone (7): This was obtained as a mixture of **2** and **7**; it was found by HLC to be identical with authentic samples. The yields were estimated from the NMR spectrum.

2-Oxo-5,5-diphenyltetrahydro-4-furancarboxylic Acid (8): Mp 191—192 °C (CCl_4); IR 1740 (COOH) and 1780 cm^{-1} (lactone); NMR ($(CD_3)_2SO$) δ=2.78 (2H, m, $-CH_2-$), 4.29 (1H, dd, –CH–) (AB_2 system, J_{AB}=6.3 Hz), and 7.1—7.8 (10H, m, 2×Ph); MS *m/e* 282 (5%, M^+), 238 (5%), 183 (100%), 105 (50%), and 77 (20%). Found: C, 72.01; H, 4.89%. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%.

5,5-Diphenyltetrahydro-2-furanone (11): Mp 90 °C (EtOH) (lit,[9] mp 90 °C); IR 1778 cm^{-1} (lactone); NMR (CCl_4) δ= 2.2—3.0 (4H, m, $-CH_2-CH_2-$), and 7.25 (10H, m, 2×Ph).

We wish to thank Professor Hideto Shosenji of the Department of Synthetic Chemistry, Faculty of Technology, Kumamoto University, for his measurement of the 100 MHz ^1H NMR spectrum, and Dr. Shinzaburo Hishida of the Hitachi Co. Ltd., Katsuda, and Mr. Shuichi Ueda at the Taiho Pharmaceutical Co. Ltd., Tokushima, for their measurements of the MS spectra. We also wish to thank Professor John F. W. McOmie for his helpful discussion and for reading the manuscript.

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