Manganese(III)-Mediated Oxidative Annulation of Methylenecyclopropanes with 1,3-Dicarbonyl Compounds

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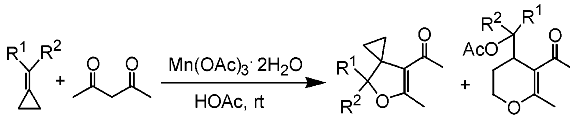

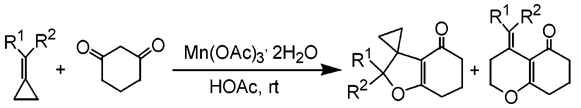

Manganese(III)-mediated oxidative annulation of methylenecyclopropanes with 1,3-dicarbonyl compounds in acetic acid produces 4,5-dihydrofuran derivatives as [3+2] annulation products in moderate to good yields under mild conditions. The possible reaction mechanism is discussed on the basis of previous mechanistic investigation.

Introduction

Methylenecyclopropanes (MCPs) **1** are highly strained but readily accessible molecules that have served as useful building blocks in organic synthesis. MCPs **1** undergo a variety of ring-opening reactions because the relief of ring strain provides a potent thermodynamic driving force.[1]

Transition metal (such as Pd, Rh, Ru, and Pt) catalyzed reactions of MCPs **1** with various reactants have attracted much attention.[2,3] In the field of Lewis-acid-catalyzed ring-opening reactions of MCPs **1** in this laboratory, we have found that the ring of MCPs **1** can be opened by alcohols and other nucleophiles in a different, novel manner to give the corresponding homoallylic derivatives in good yields under mild conditions.[4] To explore the further transformation of **1**, we investigated the radical reaction pattern of **1**.[5] Herein, we wish to report manganese(III)-mediated oxidative cyclization reactions of **1** with 1,3-dicarbonyl compounds in acetic acid.

Results and Discussion

Mn(III)-mediated oxidative free radical reactions have been extensively developed in the past two decades. They have been well demonstrated to be a valuable method for the formation of carbon−carbon bonds. Numerous regio-, chemo-, and stereoselective synthetic methods have been developed in both inter- and intramolecular reactions, and their applicability to the construction of

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(1) Synthesis of MCPs: (a) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589−635. (b) *Houben-Weyl*: *Carbocyclic Three-Membered Ring Compounds*; de Meijere, A., Ed.; Thieme: Stuttgart, Germany, 1996; Vol. E 17a−c. (c) For a recent review: Nakamura, I.; Yamamoto, Y. *Adv. Synth.*, *Catal.* **2002**, *344*, 111−129.

(2) Three types of ring-opening reaction of MCPs have been disclosed (see ref 4a). For the ring-opening of MCPs by type I, please see: (a) Camacho, D. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Angew. Chem.*, *Int. Ed. Engl.* **1999**, *38*, 3365−3367. (b) Camacho, D. H.; Nakamura, I.; Saito, S. Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 270−275. (c) Nakamura, I.; Itagaki, H.; Yamamoto, Y. *J. Org. Chem.* **1998**, *63*, 6458−6459. (d) Nüske, H.; Notlemeyer, M.; de Meijere, A. *Angew. Chem.*, *Int. Ed.* **2001**, *40*, 3411−3413. (e) Bräse, S.; de Meijere, A. *Angew. Chem.*, *Int. Ed. Engl.* **1995**, *34*, 2545−2547. (f) Tsukada, N.; Shibuya, A.; Nakamura, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8123−8124. (g) Inoue, Y.; Hibi, T.; Sataka, H.; Hashimoto, H. *Chem. Commun.* **1979**, 982−982. (h) Binger, P.; Germer, A. *Chem. Ber.* **1981**, *114*, 3325−3335. (i) Nakamura, I.; Oh, B. H.; Saito, S.; Yamamoto, Y. *Angew. Chem.*, *Int. Ed.* **2001**, *40*, 1298−1300. (j) Oh, B. H.; Nakamura, I.; Saito, S.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 6203−6205. For the ring-opening of MCPs by type II or III, please see: (k) Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Y. K.; Donskaya, N. A.; Tveritinova, E. V.; Yur'eva, N. M.; Beletskaya, I. P. *J. Org. Chem.* **1997**, *62*, 6069−6076. (l) Lautens, M.; Meyer, C.; Lorenz, A. *J. Am. Chem. Soc.* **1996**, *118*, 10676−10677. (m) Ishiyama, T.; Momota, S.; Miyaura, N. *Synlett* **1999**, 1790−1792. (n) Suginome, M.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **2000**, *122*, 11015−11016. (o) Chatani, N.; Takaya, H.; Hanafusa, T. *Tetrahedron Lett.* **1988**, *29*, 3979−3982. (p) The metal-catalyzed cocyclization reactions of MCPs with unsaturated carbon bonds have been extensively studied; please see the review: Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92. (q) Ohta, T.; Takaya, H. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, UK, 1991; Vol. 5, pp 1185−1196. (r) Binger, P.; Schmidt, T. In *Houben-Weyl*: *Methods of Organic Chemistry*; de Meijere, A., Ed.; Thieme: Stuttgart, Germany, 1997; Vol. E 17c, pp 2217−2294. (s) Binger, P.; Buch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77−151.

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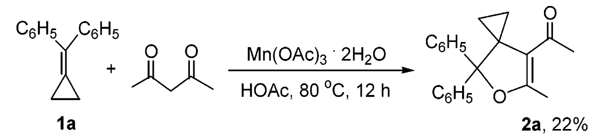
SCHEME 1. Mn(III)-Mediated Reaction of MCP 1a (1.0 equiv) with 2,4-Pentanedione (1.2 equiv) in Acetic Acid



complex natural and biologically active compounds has been demonstrated.[6] Thus, we attempted to utilize 2,4-pentanedione and 1,3-cyclohexanedione as substrates to react with MCPs **1** in the presence of $Mn(OAc)_3{\cdot}2H_2O$ in acetic acid.

As a first try, we searched for a protocol of the manganese(III)-mediated reaction of diphenylmethylenecyclopropane (**1a**) (1.0 equiv) with 2,4-pentanedione (1.2 equiv). We were pleased to find that the manganese(III) (2.2 equiv)-mediated reaction of **1a** with 2,4-pentanedione in acetic acid proceeded smoothly at 80 °C to give the cyclized product **2a** in 22% yield after 12 h (Scheme 1). The structure of **2a** was unambiguously characterized by its X-ray diffraction analysis. The ORTEP drawing of **2a** is shown in Figure 1.[7]

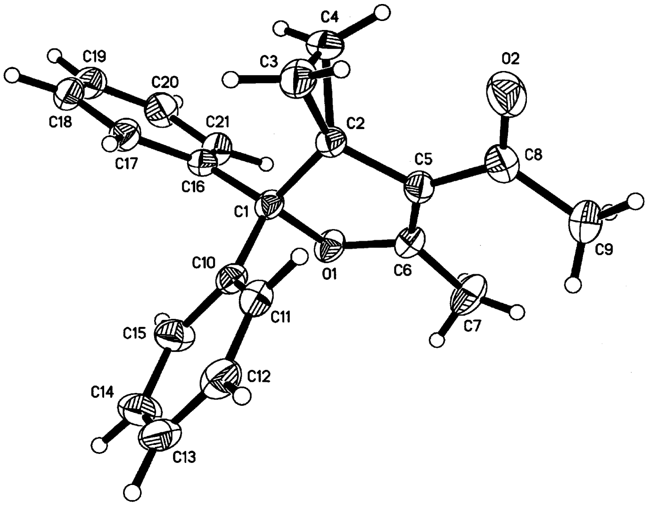


FIGURE 1. The ORTEP drawing of **2a**.

TABLE 1. Mn(III)-Mediated Reaction of MCP 1a (1.0 equiv) with 2,4-Pentanedione under Various Conditions

entry[a]	reaction conditions 2,4-pentanedione/temp/solvent	time/h	yield of **12a**/%[b]
1	1.2 equiv/80 °C/HOAc	12	22
2	1.2 equiv/rt/HOAc	12	48
3	3.0 equiv/rt/HOAc	12	50
4	2.0 equiv/rt/HOAc	12	54
5	3.0 equiv/60 °C/HOAc	12	60
6	3.0 equiv/$Cu(OAc)_2$ (2.0 equiv)/HOAc[c]	48	trace
7	3.0 equiv/$(NH_4)_2Ce(NO_3)_6$ (2.0 equiv)/HOAc[c]	48	trace
8	3.0 equiv/$K_3Fe(CN)_6$ (2.0 equiv)/HOAc[c]	48	trace
9	4.0 equiv/rt/$CHCl_3$	48	trace
10	4.0 equiv/rt/MeOH	48	trace
11	4.0 equiv/rt/1,4-dioxane	48	trace
12	4.0 equiv/rt/DMF	48	trace
13	4.0 equiv/rt/MeCN	48	trace

[a] All reactions were carred out with 2.2 equiv of $Mn(OAc)_3{\cdot}2H_2O$ under argon atmosphere. [b] Isolated yields. [c] Non-$Mn(OAc)_3{\cdot}2H_2O$ catalyst was used.

To improve the yield of **2a**, we next investigated the effects of solvents, other oxidants, reaction temperatures, and the ratios of 2,4-pentanedione to **1a** on this novel oxidative cyclization to optimize the reaction conditions. The results are summarized in Table 1. As can be seen from Table 1, at room temperature (20 °C) under the same conditions, the yield of **2a** reached 48% or 50% with use of 1.2 or 2.0 equiv of 2,4-pentanedione, respectively (Table 1, entries 2 and 3). With 3.0 equiv of 2,4-pentanedione, **2a** was obtained in 60% yield (Table 1, entry 5). At higher temperature (60 °C) under otherwise identical conditions, **2a** was obtained in 54% yield (Table 1, entry 4). The oxidant $Cu(OAc)_2$ showed no catalytic activity for this reaction under similar conditions (Table 1, entry 6). In addition, by means of other oxidants such as ammonium cerium(IV) nitrate [$(NH_4)_2Ce(NO_3)_6$] (CAN) or potassium ferricyanide(III) [$K_3Fe(CN)_6$], a trace of **2a**

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(3) For some more recent papers related to MCPs, please see: (a) Nötzel, M. W.; Rauch, K.; Labahn, T.; de Meijere, A. *Org. Lett.* **2002**, *4*, 839–841. (b) Takauchi, D.; Dsakada, K. *Chem. Commun.* **2002**, 646–647. (c) de Meijere, A.; Leonov, A.; Heiner, T.; Noltemeyer, M.; Bes, M. T. *Eur. J. Org. Chem.* **2003**, 472–478. (d) Belov, V. N.; Savchenko, A. I.; Sokolov, V. V.; Straub, A.; de Meijere, A. *Eur. J. Org. Chem.* **2003**, 551–561. (e) de Meijere, A.; Kuchuk, I. D.; Sokolov, V. V.; Labahn, T.; Rauch, K.; Es-Sayed, M.; Krämer, T. *Eur. J. Org. Chem.* **2003**, 985–997. (f) Siriwardana, A. I.; Nakamura, I.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 4547–4550. (g) Shi, M.; Shao, L.-X.; Xu, B. *Org. Lett.* **2003**, *5*, 579–582. (h) Shao, L.-X.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 963–966. (i) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213–1269. (j) Siriwardana, A. I.; Nakamura, I.; Yamamoto, Y. *Tetrahedron Lett.* **2003**, *44*, 985–990.

(4) (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145–2148. (b) Shi, M.; Chen, Y.; Xu, B.; Tang, J. *Tetrahedron Lett.* **2002**, *43*, 8019–8024. (c) Peron, G. L. N.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **2000**, *41*, 1615–1618. (d) Peron, G. L. N.; Norton, D.; Kitteringham, J.; Kilburn, J. D. *Tetrahedron Lett.* **2001**, *42*, 347–349. (e) Patient, L.; Berry, M. B.; Kilburn, J. D. *Tetrahedron Lett.* **2003**, *44*, 1015–1017. (f) Xu, B.; Shi, M. *Org. Lett.* **2003**, *5*, 1415–1418. (g) Shao, L.-X.; Shi, M. *Eur. J. Org. Chem.* **2004**, 426–430. (h) Bottini, A. T.; Cabral, L. I. *Tetrahedron* **1978**, *34*, 3187–3194. (i) Kozhushkov, S.; Spätch, T.; Fiebig, T.; Galland, B.; Ruasse, M.-F.; Xavier, P.; Apeloig, Y.; de Meijere, A. *J. Org. Chem.* **2002**, *68*, 4100–4114 and references therein. (j) Nakamura, I.; Kamada, M.; Yamamoto, Y. *Tetrahedron Lett.* **2004**, *45*, 2903–2906.

(5) For the radical reactions related with MCPs, see: (a) Mizuno, K.; Nire, K.; Sugita, H.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 6563–6566. (b) Mizuno, K.; Maeda, H.; Sugita, H.; Nishioka, S.; Hirai, T.; Sugimoto, A. *Org. Lett.* **2001**, *3*, 581–584. (c) Legrand, N.; Quiclet-Sire, B.; Zard, S. Z. *Tetrahedron Lett.* **2000**, *41*, 9815–9818. (d) Destabel, D.; Kilburn, J. D.; Knight, J. *Tetrahedron* **1994**, *50*, 11267–11288. (e) Boffey, R. J.; Santagostino, M.; Kilburn, J. D.; Whittingham, W. G. *Chem. Commun.* **1998**, 1875–1876. (f) Boffey, R. J.; Whittingham, W. G.; Kilburn, J. D. *J. Chem. Soc., Perkin Trans. 1* **2001**, 487–496. (g) Kozhushkov, S. I.; Brandl, M.; de Meijere, A. *Eur. J. Org. Chem.* **1998**, 1535–1542. (h) Xu, B.; Chen, Y.; Shi, M. *Tetrahedron Lett.* **2002**, *43*, 2781–2784. (i) De Lijser, H. J. P.; Cameron, T. S.; Arnold, D. R. *Can. J. Chem.* **1997**, *75*, 1795–1809. For reviews of radical reactions see: (j) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1237–1286. (k) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339–364. (l) *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001.

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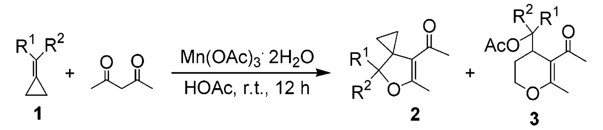
(7) The crystal data of **2a** have been deposited in CCDC with number 232276. Empirical formula, $C_{21}H_{20}O_2$; formula weight, 304.37; crystal color/habit: colorless/prismatic; crystal dimensions, 0.290 × 0.288 × 0.213 mm^3; crystal system, monoclinic; lattice type, primitive; lattice parameters, $a = 10.1025(11)$ Å, $b = 12.1715(12)$ Å, $c = 13.6175(14)$ Å, $\alpha = 90°$, $\beta = 99.925(2)°$, $\gamma = 90°$, $V = 1649.4(3)$ Å^3; space group, $P2(1)/n$; $Z = 4$; $D_{calc} = 1.226$ g/cm^3; $F_{000} = 648$; diffractometer, Rigaku AFC7R; residuals R/R_w, 0.0511/0.0854.

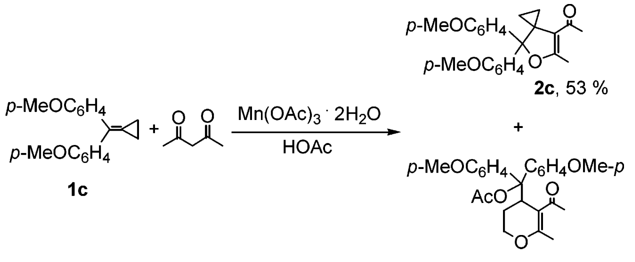
TABLE 2. $Mn(OAc)_3$-Mediated Reaction of 2,4-Pentanedione (3.0 equiv) with Various MCPs 1 (1.0 equiv)



entry	R¹/R² 1	yield [%]ᵃ 2	 3
1	p-MeC$_6$H$_4$/p-MeC$_6$H$_4$ **1b**	**2b**, 72	trace
2	p-MeOC$_6$H$_4$/p-MeOC$_6$H$_4$ **1c**	**2c**, 53	**3c**, 23^b
3	p-ClC$_6$H$_4$/p-ClC$_6$H$_4$ **1d**	**2d**, 55	trace
4	p-FC$_6$H$_4$/p-FC$_6$H$_4$ **1e**	**2e**, 77	trace
5	p-MeOC$_6$H$_4$/C$_6$H$_5$ **1f**	**2f**, 67	trace
6	o-ClC$_6$H$_4$/C$_6$H$_5$ **1g**		
7	p-EtOC$_6$H$_4$/Me **1h**	**2h**, 50^c	trace

[a] Isolated yields. [b] Isolated together with 23% ring-opened product. [c] The reaction was carried out for 24 h.

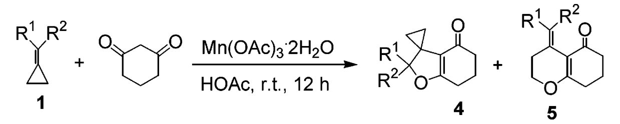
SCHEME 2. $Mn(OAc)_3$-Mediated Reaction of 2,4-Pentanedione (3.0 equiv) with MCP 1c (1.0 equiv)



was formed (Table 1, entries 7 and 8). In other organic solvents such as N,N-dimethylformamide (DMF), acetonitrile (MeCN), methanol (MeOH), 1,4-dioxane, or chloroform ($CHCl_3$) with $Mn(OAc)_3 \cdot 2H_2O$ as catalyst, a trace of **2a** was formed even in the presence of 4.0 equiv of 2,4-pentanedione (Table 1, entries 9−13). Overall, the best reaction conditions are to carry out this reaction in HOAc with 3.0 equiv of 2,4-pentanedione and 2.2 equiv of $Mn(OAc)_3 \cdot 2H_2O$ at room temperature (Table 1, entry 5).

Under the optimized reaction conditions, we next examined the Mn(III)-mediated reactions of a variety of MCPs **1** with 2,4-pentanedione in HOAc. The results are summarized in Table 2. In all the cases tested, the corresponding [3+2] cycloaddition products **2** were achieved in moderate to good yields under mild conditions (Table 2, entries 1−5 and 7). For unsymmetrical MCPs **1f** and **1h**, the corresponding cyclized products **2f** and **2h** were also obtained in good yields (Table 2, entries 5 and 7). Their spectroscopic data are summarized in the Supporting Information. For MCP **1c** [bis(p-methoxyphenyl)methylenecyclopropane], product **3c** derived from the ring-opening reaction of cyclopropane was formed along with the [3+2] annulation product **2c** (Table 2, entry 2) (Scheme 2). For MCP **1g** bearing a substituent on the ortho-position of the benzene ring, no reaction occurred under identical conditions presumably due to steric hindrance on cyclization (Table 2, entry 6).

TABLE 3. $Mn(OAc)_3$-Mediated Reaction of 1,3-Cyclohexanedione (1.2 equiv) with Various MCPs 1 (1.0 equiv)



entry	R¹/R² 1	yield [%]ᵃ 4	 5
1	C$_6$H$_5$/C$_6$H$_5$ **1a**	**4a**, 79	**5a**, trace
2	p-MeC$_6$H$_4$/p-MeC$_6$H$_4$ **1b**	**4b**, 72	**5b**, trace
3	p-MeOC$_6$H$_4$/p-MeOC$_6$H$_4$ **1c**	**4c**, 44	**5c**, 25
4	p-ClC$_6$H$_4$/p-ClC$_6$H$_4$ **1d**	**4d**, 87	**5d**, 6
5	p-FC$_6$H$_4$/p-FC$_6$H$_4$ **1e**	**4e**, 71	**5e**, 11
6	p-MeOC$_6$H$_4$/C$_6$H$_5$ **1f**	**4f**, 65	**5f**, 7
7	p-EtOC$_6$H$_4$/Me **1g**	**4g**, 40	**5g-1**, 12^{b,c} **5g-2**^{b,c}
8	p-MeOC$_6$H$_4$/H **1h**	**4h**, 30^c	**5h**, trace

[a] Isolated yields. [b] See Figure 2. [c] The reaction was carried out for 24 h.

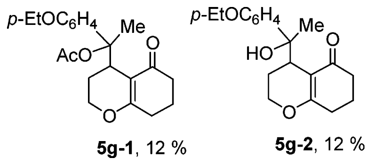


FIGURE 2. The structures of **5g-1** and **5g-2**.

Using the more reactive 1,3-cyclohexanedione as a substrate instead of 2,4-pentanedione in this oxidative annulation reaction, we found that the corresponding [3+2] cycloaddition products **4** were obtained in higher yields in most cases (Table 3, entries 1−7). In the presence of 1.2 equiv of 1,3-cyclohexanedione, this reaction proceeded efficiently to give the annulation products **4** in good yields. For unsymmetrical MCPs **1f**−**h**, the corresponding [3+2] cycloaddition products **4f**−**h** were obtained in moderate to good yield as well (Table 1, entries 6−9). It should be noted that with 1,3-cyclohexanedione as a substrate, the products **5** derived from the ring-opening reaction of cyclopropane were formed along with the [3+2] annulation products **4** in many cases (Table 3, entries 3−7). In the case of MCP **1g**, the cyclopropyl ring-opened product was obtained as mixtures of **5g-1** and **5g-2** in which **5g-2** is derived from **5g-1** after workup with aqueous alkali solution (Experimental Section) (Figure 2).

It should be noted that in this Mn(III)-mediated transformation, MCPs **1** should bear one aromatic group (R^1 and/or R^2 = aromatic group) at least because for aliphatic MCP **1** ($R^1 = R^2 =$ Bu), this reaction gave many unidentified products under identical conditions and the [3+2] annulation product was not formed.

On the basis of above results and previous investigations on Mn(III)-mediated reaction,[5h−j,8] a plausible reaction mechanism could be outlined in Scheme 3. The

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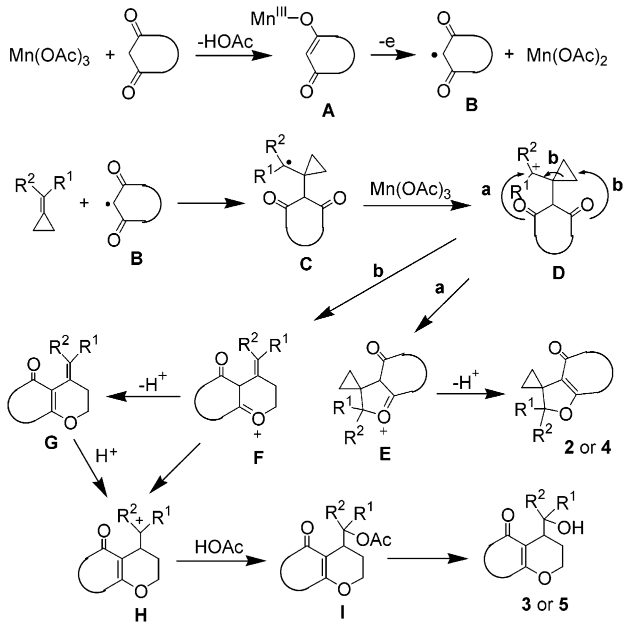
(8) Oxidation reactions of manganese(III) acetate in the formation of γ-lactones from olefins and acetic acid. See: (a) Honkanen, E.; Moisio, R.; Karvonen, P. *Acta Chem. Scand.* **1965**, *19*, 370−374. (b) Bush, J. B.; Finkbeiner, H., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 5903−5905 and references therein. (c) De Mattos, M. C. S.; De Souza, S. P. L.; Elias, S. M. *Heterocycl. Commun.* **2003**, *9*, 247−250. (d) Jogo, S.; Nishino, H.; Yasutake, M.; Shinmyozu, T. *Tetrahedron Lett.* **2002**, *43*, 9031−9034.

SCHEME 3. The Plausible Reaction Mechanism for the Formation of Annulation Products



reaction of 1,3-dicarbonyl compound with $Mn(OAc)_3{\cdot}2H_2O$ affords a Mn(III)-enolate complex **A**, which rapidly suffers electron loss to the oxo-centered Mn(III) metal system to give the radical intermediate **B**. In the presence of an alkene such as MCP **1**, the α-carbonyl radical **B** adds to the double bond of MCP **1** to furnish the radical intermediate **C**.[5i,6g] The oxidation of 1,3-dicarbonyl compound to give the complex **A** is considered as the rate-determining step.[5i,6g] This cyclopropylmethyl radical is stabilized by either two aromatic groups or at least one aromatic group of MCP **1**,[9] which does not undergo a well-known cyclopropyl ring-opened radical rearrangement.[10] Therefore, it is further oxidized by another molecule of $Mn(OAc)_3{\cdot}2H_2O$ (2.2 equiv of $Mn(OAc)_3{\cdot}2H_2O$ in the reaction system) to produce the cationic intermediate **D**, which is stabilized by the cyclopropyl and aromatic rings.[11] At any rate, this cationic intermediate **D** is more stable than the radical intermediate **C** because it is exactly a long-lived cyclopropylcarbinyl cation.[11] This should be the driving force for the transformation of **C** to **D**. The intramolecular attack of the oxygen atom in the carbonyl group via route a gives the oxonium cation **E**. Deprotonation from **E** produces the [3+2] annulation product **2** or **4**. If the intramolecular attack of the oxygen atom in the carbonyl group proceeds via route b, the cyclopropyl ring is opened and pyran oxonium cation **F** is produced. Deprotonation from cation **F** gives intermediate **G** and reprotonation affords cation **H** (this proton transformation process also can be considered to proceed directly from **F** to **H**). In acetic acid media, the acetate **I** is produced, which gives **3** or **5** after treatment with aqueous alkali solution (Scheme 3). The stability of cation **D** plays a significant role in this reaction and corresponds to this unpredictable result. Kinetically, route a is favored because the formation of oxonium cation **E** is a sterically demanding process and route b is involved with the bond cleavage along with the formation of a new double bond. Since cation **D** is stabilized in *gem*-diaryl-substituted MCPs, the major products in most cases are [3+2] annulation products and the reactions proceed smoothly. If the benzene ring bears a strongly electron-donating group, it is conceivable that cation **D** is more stabilized, which may have enough time to give the ring-opening product via route b. For mono-aryl-substituted MCPs, the corresponding cation **D** is not as stable as that in *gem*-diaryl-substituted MCPs. The reactions are somewhat sluggish and the reaction products are formed in lower yields.

Recently, Huang reported a tandem free-radical cyclization reaction of alkylenecyclopropanes with malonic acid diethyl ester mediated by Mn(III) to give 2-(3,4-dihydronaphthalen-2-yl)malonic acid diethyl ester.[12] This result is totally different from our findings in this paper with more enolizable β-dicarbonyl compounds as reactants.

In conclusion, we have found a novel radical transformation of MCPs **1** mediated by Mn(III) to give the novel [3+2] annulation compounds as major products in moderate to good yields under mild conditions.[13] The formation of a stable and long-lived cyclopropylcarbinyl cation intermediate corresponds to this unpredictable result. This finding may open a new way for the radical transformation of MCPs **1**. Efforts are underway to elucidate the mechanistic details of this Mn(III)-mediated reaction system and to extend the scope and limitations of these novel radical transformations of MCPs **1** thereof. Work along these lines is currently in progress.

Experimental Section

General Reaction Procedure for the Manganese(III)-Based Oxidative Annulation of 2,4-Pentanedione with Methylenecyclopropane 1. Under an argon atmosphere, MCP **1** (0.50 mmol), 2,4-pentanedione (1.50 mmol), and $Mn(OAc)_3{\cdot}H_2O$ (1.1 mmol) were dissolved in 5.0 mL of acetic acid. The reaction mixture was stirred at room temperature for 12 h. The reaction solution was diluted with ether (20 mL) and washed with water, saturated $NaHCO_3$ solution, brine, and water. The organic layers were dried over anhydrous Na_2SO_4.

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The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to give **2a** as a colorless solid.

1-(6-Methyl-4,4-diphenyl-5-oxa-spiro[2.4]hept-6-en-7-yl)ethanone (2a): colorless solid; yield 60%; mp 106−108 °C; IR (thin film) ν 3011, 1638, 1611, 1498, 1446, 1390, 1234 cm^{-1}; ^{1}H NMR (CDCl$_3$, TMS, 300 MHz) δ 0.23 (t, J = 4.8 Hz, 2H, CH$_2$), 1.57 (t, J = 4.8 Hz, 2H, CH$_2$), 2.24 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$), 7.25−7.35 (m, 10H, ArH); ^{13}C NMR (CDCl$_3$, TMS, 75 MHz) δ 9.0, 17.0, 30.7, 32.9, 94.8, 117.0, 127.7, 127.8, 141.7, 165.3, 193.3; MS (EI) *m/z* 304 (M$^+$) (35), 261 (27), 213 (21), 204 (23), 189 (20), 165 (21), 43 (100). Anal. Calcd for $C_{21}H_{20}O_3$: C, 82.86; H, 6.62. Found: C, 82.76; H, 6.85.

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Supporting Information Available: ^{13}C and ^{1}H NMR spectral and analytic data for compounds **2**−**5**, X-ray crystal data for **2a**, and the detailed description of experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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