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Synthesis of Dibenz[*b*,*f*]oxepins via Manganese(III)-Based Oxidative 1,2-Radical Rearrangement

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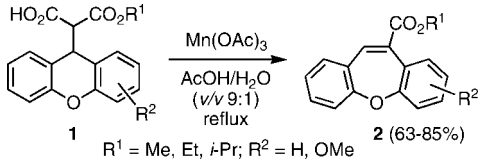

The oxidation of monoalkyl 2-(9*H*-xanthenyl)malonates **1** with $Mn(OAc)_3$ gave the 9- or 10-dibenz[*b*,*f*]oxepincarboxylates **2** in good yields. The reaction proceeds with high regioselectivity except for the case of (1-methoxyxanthenyl)malonate **1** (R^1 = Me, R^2 = 1-MeO), which gave two regioisomers. It was proposed that the process for the formation of **2** must include the 1,2-aryl radical rearrangement followed by oxidative decarboxylation.

Manganese(III) acetate, $Mn(OAc)_3$, is a versatile reagent for the C−C bond formation in organic synthesis.[1−3] In recent years, we[4] and other groups[5] have developed various Mn(III)-based oxidations of aromatic compounds in the presence of active methylene species. We previously reported that the oxidation of xanthene in the presence of dimethyl malonate mainly produced 2-(9-xanthenyl)malonate (65%) together with a small amount of 9-dibenz[*b*,*f*]oxepincarboxylate (11%) as a byproduct.[4d] Although the naturally occurring dibenz[*b*,*f*]oxepin derivatives were only found in the closely related family of the cularine alkaloids,[6] many natural products containing the skeleton were recently isolated from the rootbarks of *Artocarpus rigida*,[7] *Bauhinia saccocalyx*,[8] and *Cercis chinensis*.[9] Some of them exhibit excellent biological and pharmaceutical activities,[10] and their derivatives are widely used in industry.[11] The general strategy for the synthesis of dibenz[*b*,*f*]oxepin was mainly ascribed to two pathways involving the intramolecular C−O ether bond formation of 2-styrylphenols and the cyclodehydration of preformed diaryl ether intermediates.[6] However, both methods are conducted under harsh conditions and also include a multistep reaction process. Xanthene seems to be desirable as a readily available starting material since it only differs in a single carbon atom from dibenz[*b*,*f*]oxepin.[12] Therefore, we focused on the dibenz[*b*,*f*]oxepin isolated from the oxidation of xanthene in the presence of dimethyl malonate[4d] because the mechanism for the formation of the dibenz[*b*,*f*]oxepin as well as the skeleton was quite interesting to us. The dibenz[*b*,*f*]oxepin would probably be formed by the ring-expansion including the

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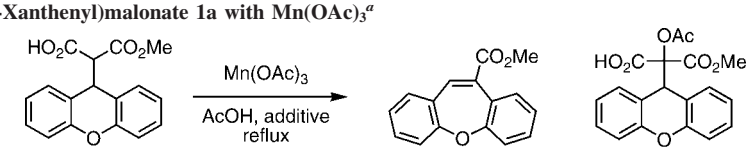
TABLE 1. Oxidation of 2-(9-Xanthenyl)malonate 1a with $Mn(OAc)_3$[a]



1a 2a 3a

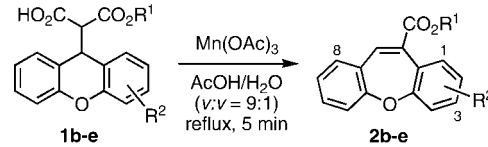
entry	1a/Mn(III)	AcOH (mL)	time (min)	additives	conv (%)	2a[b] (%)	3a[c] (%)
1	1:4	20	5	none	87	52	3
2	1:8	20	35	none	100	57	6
3	1:4	20	2.5	TFA (0.2 mL)	>99	56	36
4	1:4	20	2	TFA (1 mL)	82	37	12
5	1:4	4.5	4	H_2O (0.5 mL)	93	70	12
6	1:4	18	4	H_2O (2 mL)	96	72	14
7	1:4	10	120	H_2O (5 mL)	84	57	
8[d]	1:4	9	15	H_2O (1 mL) $Cu(OAc)_2$ (1 equiv)	100	69	
9[e]	1:4	9	5	H_2O (1 mL) $CuBr_2$ (1 equiv)	100	49	
10[f]	1:4	9	12	H_2O (1 mL) LiBr (2 equiv)	100	40	

[a] The reaction was carried out at reflux temperature at the molar ratio of **1a** (0.5 mmol):$Mn(OAc)_3$. [b] Isolated yield based on use of **1a**. [c] The acetate **3a** was obtained as an inseparable mixtuer of **1a** and the yield of **3a** was determined by the ^1H NMR spectrum. [d] 9-Xanthenone (**4**) was also isolated in an 11% yield. [e] 9-Xanthenone (**4**) and xanthene (**5**) were also isolated in 25% and 23% yields, respectively. [f] 9-Xanthenone (**4**) was also isolated in a 28% yield.

oxidative decarboxylation of the monomethyl 2-(9-xanthenyl)-malonate intermediate **1**. We then examined the reaction using malonates **1a**−**e** in order to establish the synthesis of the dibenz[*b*,*f*]oxepincarboxylates **2a**−**e** and elucidate the reaction pathway. We now report our results.

Monomethyl 2-(9-xanthenyl)malonate (**1a**) was prepared by the controlled hydrolysis of dimethyl 2-(9-xanthenyl)malonate which was prepared by the oxidation of xanthene with $Mn(OAc)_3$ in the presence of dimethyl malonate.[4d] The reaction of **1a** with $Mn(OAc)_3$ was carried out at a molar ratio of 1:4 in boiling glacial acetic acid to give methyl 9-dibenz[*b*,*f*]oxepin-carboxylate (**2a**) in 52% yield accompanied by an inseparable mixture of **1a** unchanged (13% recovered) and the acetoxylated product **3a** (3%) (Table 1, entry 1). Using 8 equiv of $Mn(OAc)_3$ led to the complete consumption of **1a** and a slight improvement in the yield of **2a** (entry 2). Based on our previous research experience[4c,d,13] and related references,[5a,14] the oxidation is sometimes affected by additives, such as sodium acetate, copper(II) acetate, water, or halide ions. Some additives promote the radical reaction in some cases, while others inhibit it. To improve the yield of **2a**, the reaction was scrutinized in the presence of various additives. Adding a small amount of trifluoroacetic acid (TFA) (*v*/*v*: AcOH/TFA = 100/1) obviously boosted the conversion of **1a**; however, a considerable amount of **3a** was produced (entry 3). Adding 1 mL of TFA (v/v: AcOH/TFA = 20/1) decreased both the conversion and the yield of **2a** (entry 4). When water was added (v/v: $AcOH/H_2O$ = 9/1), the yield of **2a** significantly increased up to 72% (entry 6). Adding a large amount of water (v/v: $AcOH/H_2O$ = 2/1) suppressed the yield of **2a** (entry 7). The combination of water and other additives, such as $Cu(OAc)_2$, $CuBr_2$, and halide ion, showed no effect or decreased the yield of **2a** together with the production of 9-xanthenone (**4**) and/or xanthene (**5**) (entries 8−10).

SCHEME 1. Oxidation of 2-(9-Xanthenyl)malonate 1b−e with $Mn(OAc)_3$



1b-e 2b-e

b: R^1 = Et, R^2 = H (63%)
c: R^1 = *i*-Pr, R^2 = H (68%)
d: R^1 = Me, R^2 = 3-MeO (81%)
e: R^1 = Me, R^2 = 1-MeO (48%)
e': R^1 = Me, R^2 = 8-MeO (37%)

The oxidation of monoethyl 2-(9-xanthenyl)malonate (**1b**) and monoisopropyl 2-(9-xanthenyl)malonate (**1c**) instead of **1a** was then carried out under the stated conditions (**1**: $Mn(OAc)_3$ = 1:4; $AcOH/H_2O$ = 9/1) to give the corresponding oxepins **2b** and **2c** in 63% and 68% yields, respectively (Scheme 1). Since the ring-enlargement reaction according to the Wagner−Meerwein rearrangement is subject to an electronic effect,[15] the oxidation of (3-methoxyxanthen-9-yl)malonate (**1d**) and (1-methoxyxanthen-9-yl)malonate (**1e**) was also examined under the standard reaction conditions (Scheme 1). To our surprise, the reaction gave completely different results. The reaction of **1d** was highly regioselective and 3-methoxydibenz[*b*,*f*]oxepin-10-carboxylate **2d** (81%) was exclusively produced. On the other hand, the reaction of **1e** gave both the 1-methoxydibenz[*b*,*f*]oxepin-10-carboxylate **2e** and 9-carboxylate **2e′** that were obtained in 48% and 37% yields, respectively. The results could probably be explained by the competition of the electronic effect and the steric effect.

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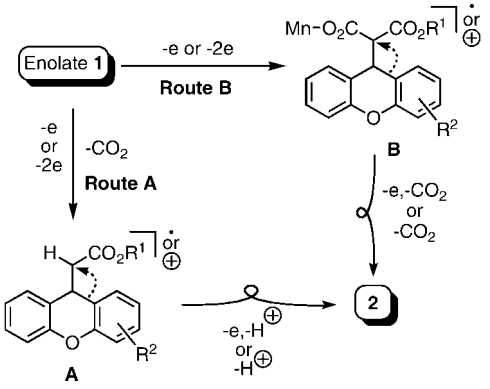
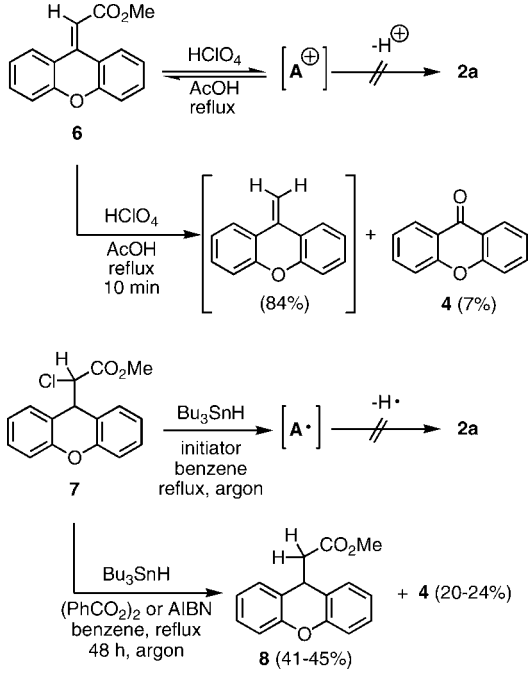
SCHEME 2. Process for the Formation of Oxepins 2 (the Oxidant Was Omitted in Each Step)

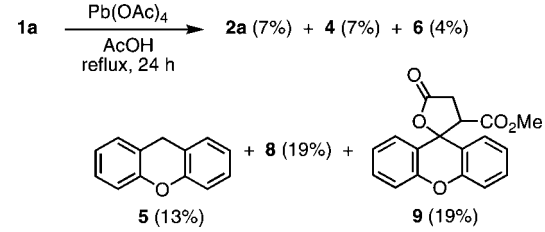


SCHEME 3. Attempt for the Formation of Oxepin 2a via the Intermediate A

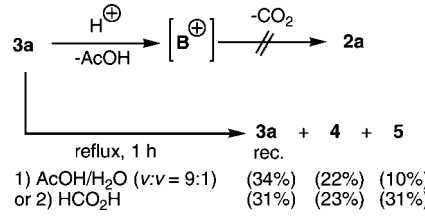


The mechanism for the formation of the dibenz[*b*,*f*]oxepins **2** deserves comment. Although the dibenz[*b*,*f*]oxepins **2** must be produced via the 1,2-aryl rearrangement, we were interested in which rearrangement occurred before (route A) or after the decarboxylation (route B) and followed by an ionic or radical process (Scheme 2). When the malonate **1a** was heated under reflux in acetic acid in the presence of $Mn(OAc)_2$ or $Cu(OAc)_2$, the decarboxylation did not occur and only **1a** was recovered. The results indicate that the decarboxylation should oxidatively proceed and $Mn(OAc)_3$ was essential for the formation of the oxepin **2**. In order to examine the rearrangement after the decarboxylation (route A), methyl (9-xanthenylidene)acetate (**6**), prepared by the Reformatsky reaction of α-bromoacetate in the presence of Zn followed by hydrolysis or the oxidation of **1a** with DDQ then by hydrolysis, was treated with perchloric acid (upper reaction in Scheme 3). However, the acid-catalyzed reaction did not give **2a** via the cation equivalent **A**, but 9-methylenexanthene[16] and **4** in 84% and 7% yields, respectively. In addition, chloro(9-xanthenyl)acetate **7** prepared by the reaction of 9-xanthenol with α-chloromalonate was allowed to react with Bu_3SnH in the hope of forming the radical equivalent **A** which might afford **2a** (lower in Scheme 3). However, the reaction only gave the corresponding xanthenylacetate **8** (41−45%) and **4** (20−24%) together with **7** unchanged (25−30%). On the other hand, the oxidative decarboxylation of **2a** using $Pb(OAc)_4$ was examined in order to form the intermediate radical **A**.[17] As a result, although the reaction was very complicated, the products **4**, **5**, **6**, **8**, and spirolactone **9** were obtained together with only a small amount of the oxepin **2a** (Scheme 4).[18] These results supported the fact that the 1,2-aryl rearrangement should occur before the decarboxylation (route B), and the rearrangement after the decarboxylation according to route A seemed to be unlikely in the present $Mn(OAc)_3$ oxidation (Scheme 2).

SCHEME 4. Oxidation of 1a with $Pb(OAc)_4$



SCHEME 5. Reaction of 3a under Acidic Conditions



We next explored the rearrangement before the decarboxylation via route B. Since the intermediate cation **B** in Scheme 2 seemed to be equivalent to the cation produced by the acid-catalyzed deacetoxylation of the byproduct **3a**, the reaction of **3a** was carried out under acidic conditions (Scheme 5).[15] However, the reaction did not give **2a**, but 9-xanthenone (**4**) and xanthene (**5**) along with **3a** unchanged. Therefore, the ionic rearrangement containing the corresponding cation **B** in Scheme 2 should be ruled out. In order to confirm the formation of the radical intermediate **B** before the 1,2-aryl rearrangement, we attempted trapping **B** with an alkene. When the malonate **1a** was used under similar reaction conditions in the presence of 1,1-diphenylethene, xanthenylbutanolide **10** (31%; 1:1 stereoisomer) was isolated except for the desired oxepin **2a** (Scheme 6). It is obvious that the radical intermediate **B** must be formed before the 1,2-aryl rearrangement since it is well-known that the malonic acid radical such as **B** adds alkene.[1]

(16) 9-Methylenexanthene decomposed during the separation procedure to afford **4**.

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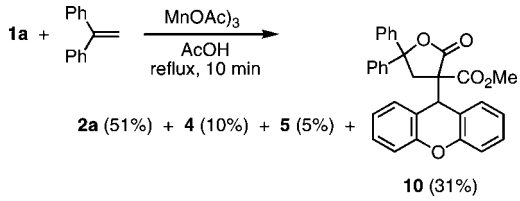
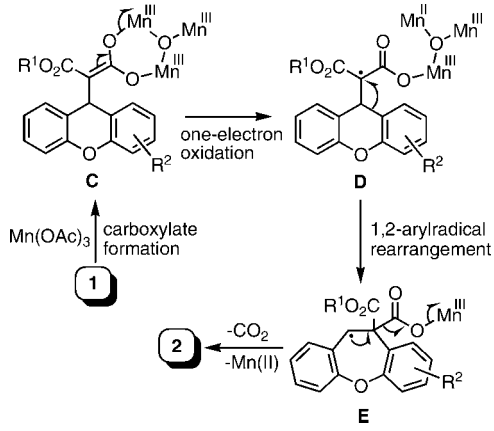
(18) Incidentally, the xanthenylidenemalonate **6** and xanthenylacetate **8** would be produced by the dehydrogenation and the hydrogen abstraction of the intermediate radical **A**, and the spirolactone **9** would be obtained by the coupling of **A** with the carboxymethyl radical, $^{\bullet}CH_2CO_2H$, followed by oxidative lactonization since the α carbonyl carbon radicals, such as **A**, could not be oxidized by $Pb(OAc)_4$, but the benzyl-type radicals, such as the 9-xanthenyl radical, could be easily oxidized.[17d,e]

SCHEME 6. Mn(III)-Based Reaction of a Mixture of 1a and Alkene



SCHEME 7. Reaction Pathway for the Formation of Oxepins 2



It was concluded that the carboxylate **C** must be formed during the first stage since the $Mn(OAc)_3$ oxidant was essential for the reaction, and then the one-electron oxidation would occur to give the α-carbonylcarbon radical **D** which should rearrange to form the more stable benzyl-type radical **E** followed by oxidative decarboxylation to finally produce the corresponding oxepins **2**. The reaction pathway is outlined in Scheme 7.

In summary, we have developed a new approach to the synthesis of the dibenz[*b*,*f*]oxepincarboxylates **2a-e** during the $Mn(OAc)_3$-mediated oxidative intramolecular rearrangement. We have also proposed the mechanism for the formation of **2** involving the 1,2-arylradical rearrangement and subsequent decarboxylation. Although the 1,2-radical rearrangement has been well-documented for the construction of medium and large rings,[19] to the best of our knowledge, the Mn(III)-promoted 1,2-aryl radical rearrangement is little known.[20]

(19) Zhang, W. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: New York, 2001; Vol. 2, pp 234−245, and references cited therein.

(20) Tsai, A.-I.; Chuang, C.-P. *Tetrahedron* **2008**, *64*, 5098–5102.

Experimental Section

General Procedure for the Oxidation of 2-(9-Xanthenyl)-malonates 1 with $Mn(OAc)_3$. To a heated solution of **1** (0.5 mmol) in glacial acetic acid (10 mL) in the presence and absence of an additive was added $Mn(OAc)_3$ (2 mmol) just before refluxing. The reaction was stopped when the dark-brown color of the solution turned clear red. The reaction mixture was then cooled to room temperature, and the solvent was removed in vacuo. The residue was triturated with 2 M (1 M = 1 mol dm^{-3}) HCl (15 mL) followed by extraction with $CHCl_3$ (10 mL × 3). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (15 mL × 2) and water (10 mL × 2). The organic layer was dried over $MgSO_4$ and again concentrated to dryness. The crude products were separated by silica gel TLC (Wako B-10) while eluting with $CHCl_3$ to give dibenz[*b*,*f*]oxepincarboxylate **2**. 9-Xanthenone (**4**) and xanthene (**5**) were also isolated in some cases. For the reaction of **1a**, the water layer was acidified with concd H_2SO_4 and then extracted with $CHCl_3$ (10 mL × 3). The extract was washed with water (20 mL × 2), dried over $MgSO_4$, and again concentrated to dryness. The crude products were not separated and the yields of **1a** and **3a** were directly estimated by the ^1H NMR spectrum.

Isopropyl 9-dibenz[*b*,*f*]oxepincarboxylate (2c): colorless microcrystal (from Et_2O−hexane); mp 74−75 °C; IR (KBr) 1705 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (1H, s), 7.53−7.14 (8H, m), 5.26 (1H, hept, J = 6.0 Hz), 1.37 (6H, d, J = 6.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 158.9, 158.7, 137.4, 131.8, 131.5, 130.6, 130.2, 128.8, 127.8, 124.9, 124.5, 121.3, 121.0, 68.9, 21.8; MS *m*/*z* (rel intensity) 280 (M^+, 100). Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.30; H, 5.64.

2-Methoxycarbonyl-4,4-diphenyl-2-(9-xanthenyl)-4-butanolide (10): one of the stereoisomers; colorless microcrystals (from EtOAc-hexane); mp 140−141 °C; IR (KBr) 1782, 1740 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39−7.05 (18H, m), 6.26 (1H, s), 3.35 (1H, d, J = 13.8 Hz), 3.23 (3H, s), 2.76 (1H, d, J = 13.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 168.8, 146.3, 143.5, 142.1, 142.0, 138.3, 130.2, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 125.3, 125.0, 124.9, 123.6, 57.9, 53.0, 45.4; MS *m*/*z* (rel intensity) 476 (M^+, 14). Anal. Calcd for $C_{31}H_{24}O_5$: C, 78.14; H, 5.08. Found: C, 77.96; H, 5.04.

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Supporting Information Available: Experimental procedures and characterization of the products **2a**−**e**, **3a**, and **6**−**10′** as well as copies of the ^1H NMR,^{13}C NMR, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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