molbank

MDPI

Communication

4-Acetyl-2-hydroxy-2,5-dimethylfuran-3(2*H*)-one

Chiaki Akazaki [1], Shun Kawabata [1] and Hiroshi Nishino [2,*]

[1] Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan; 159d8021@st.kumamoto-u.ac.jp (C.A.); 158d8027@st.kumamoto-u.ac.jp (S.K.)

[2] Department of Chemistry, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

* Correspondence: nishino@sci.kumamoto-u.ac.jp; Tel.: +81-96-342-3374

Academic Editors: Luke R. Odell and Norbert Haider

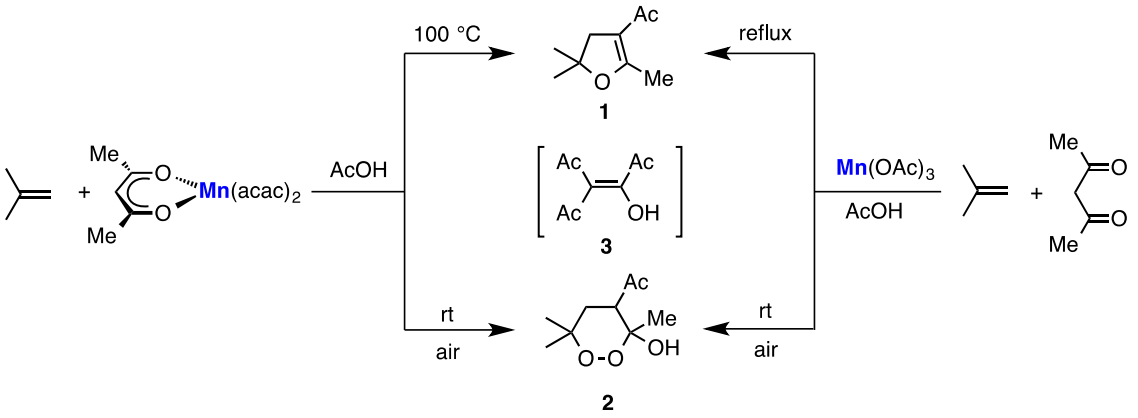
Received: 7 September 2016; Accepted: 14 October 2016; Published: 20 October 2016

Abstract: The facile synthesis of 4-acetyl-2-hydroxy-2,5-dimethylfuran-3(2*H*)-one (**4**) was achieved by the $Mn(OAc)_3$-mediated aerobic oxidation of 2,4-pentanedione or the direct reaction of $Mn(acac)_3$ in AcOH-TFE at room temperature under a dried air stream.

Keywords: 4-acetyl-2-hydroxy-2,5-dimethylfuran-3(2*H*)-one; keto-hemiacetal; $Mn(acac)_3$; $Mn(OAc)_3$; aerobic oxidation; 2,4-pentanedione; cyclic acetal; trifluoroethanol

1. Introduction

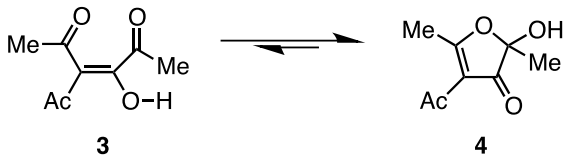
It is well-known that the oxidation of alkenes with tris(2,4-pentanedionato)manganese(III), $Mn(acac)_3$, produces dihydrofurans **1** [1], which are also produced by the oxidation of a mixture of alkenes and 2,4-pentanedione (Hacac) with manganese(III) acetate dihydrate, $Mn(OAc)_3{\cdot}2H_2O$. When the reactions are carried out at room temperature in air, 1,2-dioxan-3-ols **2** are produced [2] (Scheme 1). Both reactions would be affected by the formation of a by-product, 3-acetyl-4-hydroxyhex-3-ene-2,5-dione (**3**), which would be generated by a bimolecular coupling reaction of 2,4-pentanedione radicals [3]. However, the crystalline by-product is easy to remove from the dihydrofurans **1** and 1,2-dioxian-3-ols **2** by a chromatographic separation (Scheme 1).



Scheme 1. Synthesis of Dihydrofurans and 1,2-Dioxan-3-ols Using Mn(III) Complexes.

The by-product **3** is attractive as a synthetic building block in many organic reactions because it is an electron-deficient alkene [4–15]. Therefore, we initially investigated the reaction of ketones [16], electron-rich heterocycles, and dienes [17]. However, all the reactions failed or gave an intractable mixture. The results were very confusing, and we doubted the structure of **3** since the cyclic

keto-hemiacetal **4** should be rather more stable than the electron-deficient vinyl alcohol **3** (Scheme 2). In this paper, we discuss the characterization of the exact structure of the by-product **3**, the optimization of the aerobic oxidation reaction, and the reaction mechanism.



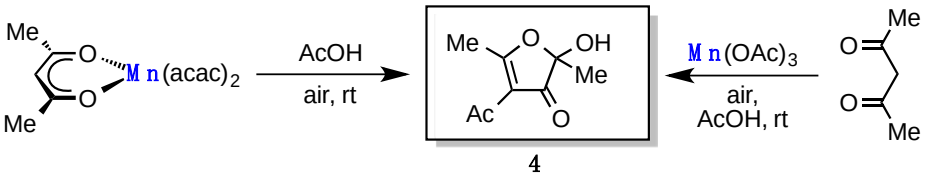
Scheme 2. Tautomerism of the by-product **3**.

2. Results

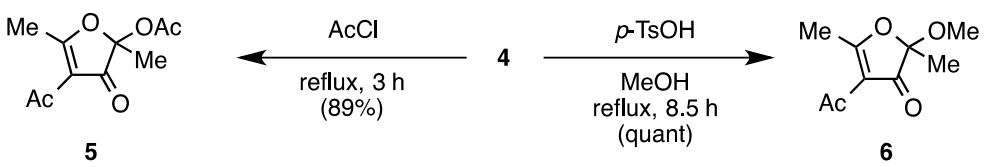
A single crystal of the by-product was successfully grown from $CHCl_3$/hexane and subjected to an X-ray crystallographic measurement. As a result, we obtained the exact structure of the compound as 4-acetyl-2-hydroxy-2,5-dimethylfuran-3(2*H*)-one (**4**) (Supplementary Materials). We were very surprised by the production of **4** and then scrutinized the reaction using Mn(III) complexes.

The reaction of $Mn(acac)_3$ or Hacac with $Mn(OAc)_3$ was carried out in acetic acid (AcOH) at room temperature in air or under an oxygen atmosphere from a mechanistic aspect [2], affording the furanone **4** in a yield similar to that reported in the literature (Scheme 3 and Table 1, Entries 2, 4, and 8) [1–3]. Removal of water led to a decreased yield (Entries 5 and 9). Although the yield did not change in the reaction using $Mn(acac)_3$ under a dried air stream (Entry 3), it dramatically increased in the reaction of Hacac with $Mn(OAc)_3$ (Entry 12). The addition of trifluoroethanol (TFE) [18–20] was fairly effective in the reaction of $Mn(acac)_3$ (Entry 6), while it dramatically improved the yield of **4** in the reaction of Hacac with $Mn(OAc)_3$ (compare Entry 8 with Entry 14). We recently found that formic acid displayed both an increasing reaction rate and product yield for the Mn(III)-based oxidative reaction [21]. The reaction was then carried out in the presence of formic acid. Unfortunately, despite acceleration of the reaction, it became complicated (Entry 10). It was also not effective to add sodium acetate (Entry 11) [22,23]. Eventually, we realized the maximum yield of **4** in the presence of trifluoroethanol under a dried air stream (Entry 15). Therefore, the optimized conditions in order to synthesize the furnone **4** in the direct method using $Mn(acac)_3$ were in AcOH-TFE at room temperature in air for 12 h (Entry 6), while the best conditions in the reaction of Hacac with $Mn(OAc)_3$ were in AcOH-TFE at room temperature under a dried air stream for 12 h (Entry 15).

In addition, the cyclic keto-hemiacetal **4** was easily transformed into the corresponding acetoxy-acetal **5** (89%) [2] and methoxy-acetal **6** (quant) (Scheme 4).



Scheme 3. Production of the furanone **4**.



Scheme 4. Conversion of the furanone **4**.

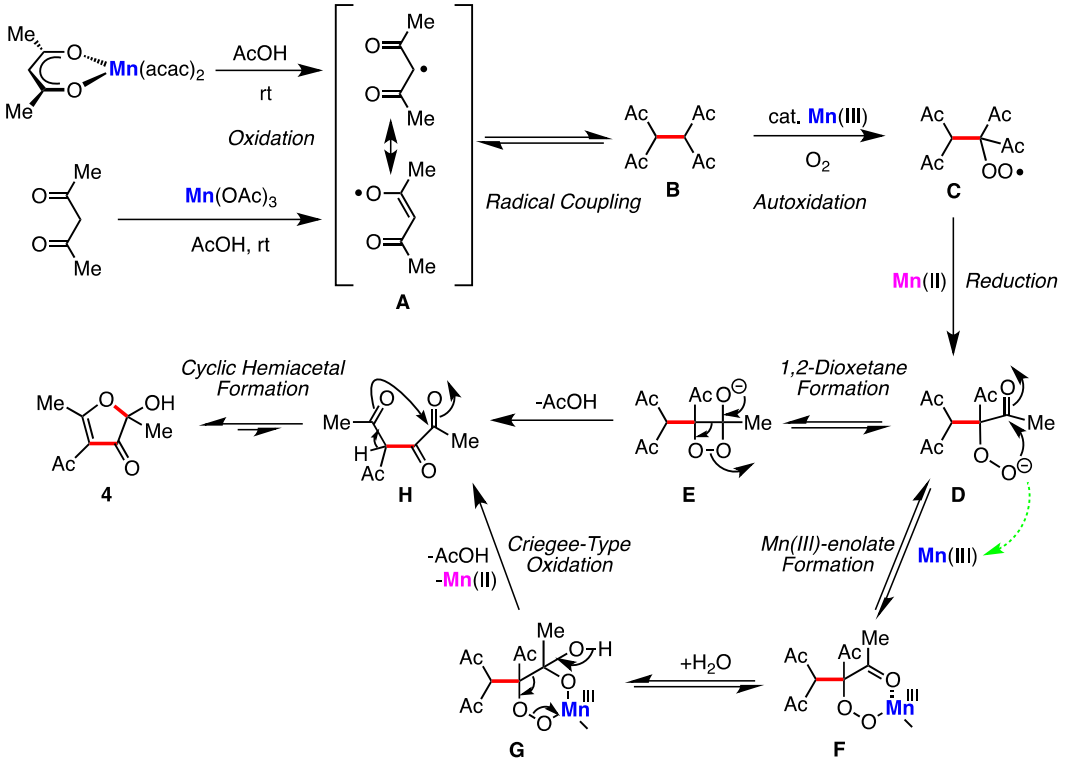
Table 1. Reaction of $Mn(acac)_3$ [1] and 2,4-Pentanedione (Hacac) with $Mn(OAc)_3$ in AcOH [2].

Entry	Conditions		Additive	Time/h	4/Yield/% [3]
1	$Mn(acac)_3$	argon		12	14
2		air		12	35
3		dried air stream		12	35
4		O_2 (1 atm)		12	39
5		O_2 (5 atm)	MS4A	6	24
6		air	CF_3CH_2OH [4]	12	44
7	$Mn(OAc)_3$/Hacac	argon		18	15
8		air		18	29
9		air	MS4A	18	14
10		air	HCO_2H [5]	3	5
11		air	NaOAc [6]	12	21
12		dried air stream		12	52
13		O_2 (1 atm)	CF_3CH_2OH [4]	12	49
14		air	CF_3CH_2OH [4]	12	58
15		dry-air stream	CF_3CH_2OH [4]	12	61

[1] $Mn(acac)_3$ (1.0 mmol) was used in AcOH (25 mL); [2] Hacac (3.0 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (1.5 mmol) were used in AcOH (15 mL); [3] Entries 1–5: Isolated yield based on $Mn(acac)_3$. Entries 6–10: Isolated yield based on Hacac; [4] AcOH:CF_3CH_2OH = 9:1 *v*/*v*; [5] AcOH:HCO_2H = 9:1 *v*/*v*; [6] NaOAc (6.0 mmol) was added.

3. Discussion

The reaction was not effective under an argon atmosphere (Table 1, Entries 1, 7), but in air, the furanone **4** was produced as the sole product. Therefore, it was considered that the reaction must proceed according to the Mn(III)-mediated aerobic oxidation [2]. The one-electron oxidation of $Mn(acac)_3$ or the manganese(III)-enolate complex formed in situ from the ligand-exchange reaction of Hacac with $Mn(OAc)_3$ [2] gave the 1,3-dicarbonyl radicals **A** (Scheme 5), which underwent a head-to-head radical coupling reaction to produce the dimeric compound **B**. The 1,3-dicarbonyl radical **A** could be trapped by a radical scavenger such as xanthene and 2,6-di-*tert*-butyl-4-methylphenol (BHT) [24]. The dimeric compound **B** should be more reactive than Hacac, thus compound **B** would be further oxidized and followed by capture of the dissolved molecular oxygen to produce the peroxy radical **C**. Radical **C** should be reduced by Mn(II), affording the peroxy anions **D** and the reproduced Mn(III) species [25,26]. The peroxy anion **D** must be converted to 4-acetylhexane-2,3,5-trione (**H**) via the 1,2-dioxetane formation [27]. Alternatively, the Mn(III)-enolate complex **F** would be formed by the reaction of the anion **D** with Mn(III) species, followed by the Criegee-type oxidation [2,28] accompanying the addition of water to also produce the trione **H** since the reaction was suppressed under dry conditions (Entries 5, 9). Eventually, the trione **H** cyclized and the stable furanone **4** was isolated. The proposed mechanism is briefly depicted in Scheme 5.



Scheme 5. Proposed mechanism for the formation of the furanone **4**.

4. Experimental

All reagents, except for $Mn(acac)_3$ and $Mn(OAc)_3{\cdot}2H_2O$, were commercially available and used without further purification. Tris(2,4-pentanedionato)manganese(III), $Mn(acac)_3$, was prepared by reaction of 2,4-pentanedione, Hacac, with potassium permanganate, $KMnO_4$ [29]. Manganese(III) acetate dihydrate, $Mn(OAc)_3{\cdot}2H_2O$, was prepared according to our modified method [16]. Flash column chromatography was performed on silica gel 60N (40–50 μm), which was purchased from Kanto Chemical Co., Inc., (Tokyo, Japan) and preparative thin layer chromatography (TLC) on Wakogel B-5F from Wako Pure Chemical Ind., Ltd. (Osaka, Japan). The solvents were commercially available first grade and used as received. Melting points were obtained using a Yanagimoto micromelting point apparatus and are uncorrected. The NMR spectra were recorded using a JNM ECX 500 spectrometer at 500 MHz for ^1H and at 125 MHz for ^{13}C (Kumamoto, Japan), with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm). The IR spectra were measured in $CHCl_3$ using a Shimadzu 8400 FT-IR spectrometer and expressed in cm^{-1} (Kumamoto, Japan). The high-resolution mass spectra and the elemental analysis were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan. The X-ray analysis was performed using a SuperNova A diffractometer with a Cu micro-focus source and the final obtained structure was of very high quality and automatically solved by the AutoChem module.

4-Acetyl-2-hydroxy-2,5-dimethylfuran-3(2H)-one (**4**) *[2,3]*

$Mn(acac)_3$ (351.1 mg) was stirred in a mixture of AcOH (22.5 mL) and TFE (2.5 mL) at room temperature in air for 12 h. The solvent was removed *in vacuo* and the residue was triturated with 2M hydrochloric acid. The obtained aqueous acidic mixture was extracted with $CHCl_3$ (20 mL × 3). The combined organic extracts were washed with aqueous $NaHCO_3$ solution, water, dried ($MgSO_4$), and then concentrated dryness. The obtained products were separated by column chromatography eluted by EtOAc–hexane (1:1 v/v), affording **4** (74.1 mg; 44%) (Table 1, Entry 6).

In contrast, Hacac (308.6 mg) and $Mn(OAc)_3 \cdot 2H_2O$ (407.1 mg) were added in a mixture of AcOH (13.5 mL) and TFE (1.5 mL), and the mixture was then stirred at room temperature under a dried air stream for 12 h. The work-up was performed by the procedure described above, giving **4** (159.4 mg; 61%) (Table 1, Entry 15).

Coloress prisms (from $CHCl_3$); mp 116.0–116.3 °C; R_f = 0.57 (EtOAc-hexane, 1:1 *v*/*v*); IR ($CHCl_3$) ν 1712, 1674 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.21 (1H, s, OH), 2.63 (3H, s, Ac), 2.43 (3H, s, CH_3), 1.62 (3H, s, CH_3); ^{1}H-NMR (500 MHz, DMSO-d_6) δ 8.06 (1H, s, OH), 2.56 (3H, s, Ac), 2.28 (3H, s, CH_3), 1.39 (3H, s, CH_3); ^{13}C-NMR (125 MHz, DMSO-d_6) δ 197.4 (C-3), 195.7 (Ac), 193.3 (C-5), 113.1 (C-4), 107.1 (C-2), 30.0 (Ac), 22.1 (CH_3), 18.8 (CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.9 (C-3), 195.9 (Ac), 194.0 (C-5), 113.0 (C-4), 105.7 (C-2), 29.7 (Ac), 21.7 (CH_3), 18.5 (CH_3); Found: C, 56.38; H, 5.95%. Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92%.

X-Ray Crystallographic Data: empirical formula $C_8H_{10}O_4$; formula weight 170.16; colorless prisms; space group $P2_1/c$; cell lengths a = 8.13551(9), b = 12.91881(9), c = 8.38084(9) Å; cell angles α = 90.00°, β = 114.5940(13)°, γ = 90.00°; cell volume 800.926 Å^3; formula units per cell Z = 4, Z' = 0; density ρ = 1.411 g/cm^3; absorption coefficient μ = 0.970; radiation (CuK_α) λ= 1.54184; R = 0.0342; R_w = 0.0860; GOF = 1.053. (CCDC 1501028 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk)).

4-Acetyl-2,5-dimethyl-3-oxo-2,3-dihydrofuran-2-yl Acetate (**5**) *[2]*

A mixture of the furanone **4** (84.8 mg) and acetyl chloride was heated under reflux for 3 h, then concentrated to dryness, giving the acetate **5** (74.3 mg; 70%) (89% yield based on the ^{1}H-NMR spectrum). The acetate **5** was easily hydrolyzed during the work-up, yielding a mixture of the furanone **4**.

Pale yellow liquid; R_f = 0.36 (EtOAc-hexane, 2:8 *v*/*v*); IR ($CHCl_3$) ν 1768, 1723, 1687 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.58 (3H, s, Ac), 2.45 (3H, s, CH_3), 2.13 (3H, s, OAc), 1.58 (3H, s, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 195.0 (C-3), 193.8 (Ac), 193.2 (C-5), 114.3 (C-4), 102.1 (C-2), 29.8 (Ac), 21.0 (CH_3), 20.2 (OAc), 17.6 (CH_3); FAB HRMS (acetone/NBA): calcd for $C_{10}H_{12}O_5$ 212.0688 (M); found 212.0685.

4-Acetyl-2-methoxy-2,5-dimethylfuran-3(2H)-one (***6***)

The franone **4** (744.4 mg) and *p*-toluenesulfonic acid (84.9 mg) were heated under reflux in MeOH (20 mL) for 8.5 h and aqueous $NaHCO_3$ solution (20 mL) was then added to the mixture. The aqueous solution was extracted with $CHCl_3$ (20 mL × 3) and the combined organic extracts were dried ($MgSO_4$) and then concentrated dryness, quantitatively giving the liquid methoxy-acetal **6** (802.6 mg; quant).

Pale yellow liquid; R_f = 0.52 (EtOAc-hexane, 2:8 *v*/*v*); IR ($CHCl_3$) ν 1712, 1674 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.28 (3H, s, OCH_3), 2.68 (3H, s, Ac), 2.46 (3H, s, CH_3), 1.55 (3H, s, CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.3 (C-3), 196.1 (Ac), 193.3 (C-5), 114.7 (C-4), 109.0 (C-2), 52.3 (OMe), 29.8 (Ac), 20.8 (CH_3), 18.1 (CH_3); FAB HRMS (acetone/NBA): calcd for $C_9H_{13}O_4$ 185.0814 (M + H); found 185.0804.

5. Conclusions

It was confirmed that the product obtained by the oxidation of $Mn(acac)_3$ or Hacac with $Mn(OAc)_3$ in AcOH was not 3-acetyl-4-hydroxyhex-3-ene-2,5-dione (**3**), but 4-acetyl-2-hydroxy-2,5-dimethylfuran-3(2*H*)-one (**4**), of which the best yield was accomplished by the reaction at room temperature under a dried air stream in AcOH-TFE. In addition, we proposed the mechanism for the formation of **4**. Recently, Wu et al. also reported the isolation of the furanone **4** by the extremely complicated polyoxometalates-catalyzed oxidation of Hacac with hydrogen peroxide [30]. However,

they did not mention the formation mechanism. The present method is superior in view of the synthesis of **4** than Wu's because of a very easy handling procedure using commercially-available simple materials [31] under mild conditions, such as room temperature in air, in addition to a synthetically acceptable yield, and the reaction using various 1,3-dicarbonyl derivatives are currently underway in our laboratory. A similar compound, ethyl 2-(2-hydroxy-3-oxo-5-phenyl-2,3-dihydrofuran-2-yl)acetate, is also known [32], which was prepared by condensation of ethyl acetate with diethyl oxalate and acetophenone.

Supplementary Materials: The followings are available online at http://www.mdpi.com/1422-8599/2016/4/M913, ^{1}H-NMR, ^{13}C-NMR, and IR spectra, ORTEP drawing and cif of **4**; ^{1}H-NMR and ^{13}C-NMR spectra of **5**; ^{1}H-NMR, ^{13}C-NMR, DEPT, IR, and FAB MS spectra of **6**.

Acknowledgments: This research was supported by a Grant-in-Aid for Scientific Research (C), No. 25410049, from the Japan Society for the Promotion of Science. We also acknowledge Nissan Chemical Industries, Ltd., and Astellas Foundation for Research on Metabolic Disorders for their financial support.

Author Contributions: H.N. conceived and designed the experiments; C.A. and S.K. performed the experiments; H.N. analyzed the data, contributed reagents/materials/analysis tools, and wrote the manuscript. All authors read and approved the final manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Nishino, H. The Facile Synthesis of Dihydrofurans by the Oxidation of Olefins with Tris(2,4-pentanedionato) manganese(III). *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1922–1927. [CrossRef]
2. Nishino, H.; Tategami, S.; Yamada, T.; Korp, J.D.; Kurosawa, K. Formation of 1,2-Dioxanes by the Use of Tris(2,4-pentanedionato)manganese(III) or Manganese(III) Acetate. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1800–1809. [CrossRef]
3. Nishino, H. Direct Diacetylmethylation of Aromatic Compounds with Tris(2,4-pentanedionato) manganese(III). *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1733–1739. [CrossRef]
4. Chechina, N.V.; Zubar, V.V.; Omelchenko, I.V.; Kolos, N.N. One-pot synthesis of new derivatives of 3,4-dihydropyrimidinone, and substituted imidazolin-2-ones. *ARKIVOC* **2015**, 293–304.
5. Ni, F.; Yang, Y.; Shu, W.-M.; Ma, J.-R.; Wu, A.-X. Brønsted acid promoted addition–cyclization and C–C bond cleavage: A convenient synthesis of 2-amino-5-aroylmethylthiazoles derivatives. *Org. Biomol. Chem.* **2014**, *12*, 9466–9470. [CrossRef] [PubMed]
6. Yang, Y.; Ni, F.; Shu, W.-M.; Wu, A.-X. Water as an additive for selective synthesis of saturated 1,4-diketones and tetrasubstituted furans directly from 1,4-enediones. *Tetrahedron* **2014**, *70*, 6733–6741. [CrossRef]
7. Shu, W.-M.; Yang, Y.; Zhang, D.-X.; Wu, L.-M.; Zhu, Y.-P.; Yin, G.-D.; Wu, A.-X. Highly Efficient Synthesis of 3a,6a-Dihydrofuro[2,3-*b*]furans via a Novel Bicyclization. *Org. Lett.* **2013**, *15*, 456–459. [CrossRef] [PubMed]
8. Yang, Y.; Gao, M.; Wu, L.-M.; Deng, C.; Zhang, D.-X.; Gao, Y.; Zhu, Y.-P.; Wu, A.-X. A facile synthesis of indole-furan conjugates via integration of convergent and linear domino reactions. *Tetrahedron* **2011**, *67*, 5142–5149. [CrossRef]
9. Quast, H.; Seefelder, M.; Ivanova, S.; Heubes, M.; Peters, E.-M.; Peters, K. Tetraacylethenes as Dienophiles and Hetero Dienes in Two-Step Diels–Alder Reactions. *Eur. J. Org. Chem.* **1999**, 3343–3351. [CrossRef]
10. Adembri, G.; Celli, A.M.; Lampariello, L.R.; Scotton, M.; Sega, A. A new route to highly substituted 1*H*-pyrrol-3(2*H*)-ones. *Tetrahedron Lett.* **1994**, *35*, 4023–4026. [CrossRef]
11. Celli, A.M.; Lampariello, L.R.; Scotton, M.; Sega, A. Reaction of 3,4-diacetylethylenes with enamines and Schiff bases. Synthesis of furo-furan and furo-oxazole derivatives. *Gazz. Chim. Ital.* **1993**, *123*, 543–547. [CrossRef]
12. Celli, A.; Scotton, M.; Sega, A. Synthesis of furo-furans by rearrangement of 4-acetylpyrans. *Tetrahedron* **1992**, *48*, 5883–5900. [CrossRef]
13. Adembri, G.; Di Tommaso, A.; Lampariello, L.R.; Scotton, M. Tetraacetylethylene and nitrile oxides: Synthesis of spirofuranisoxazoles. *J. Heterocycl. Chem.* **1988**, *25*, 1621–1625. [CrossRef]
14. Adembri, G.; Anselmi, C.; Celli, A.M.; Lampariello, L.R.; Scotton, M. Facile synthesis of 5-(α-alkyl-substituted) furans. *J. Heterocycl. Chem.* **1984**, *21*, 569–571. [CrossRef]

15. Graziano, M.L.; Iesce, M.R.; Carli, B.; Scarpati, R. Photosensitized Oxidation of Furans; VI. A Simple General Method for the Synthesis of Functionalized *cis*-1,2-Diacylethylenes (2-Ene-1,4-diones). *Synthesis* **1983**, 125–126. [CrossRef]
16. Onitsuka, S.; Nishino, H.; Kurosawa, K. Acid-Catalyzed Convenient Transformation of 1-Aryl-2-pentene-1,4-diones into Polyfunctionalized Furans. *Tetrahedron Lett.* **2000**, *41*, 3149–3152. [CrossRef]
17. Onitsuka, S.; Nishino, H. Synthesis of Polyfunctionalized Furans from 1-Aryl-2-pentene-1,4-diones. *Tetrahedron* **2003**, *59*, 755–765. [CrossRef]
18. Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. Hypervalent Iodine-Induced Nucleophilic Substitution of *para*-Substituted Phenol Ethers. Generation of Cation Radicals as Reactive Intermediates. *J. Am. Chem. Soc.* **1994**, *116*, 3684–3691. [CrossRef]
19. Dohi, T.; Murayama, A.; Minamitsuji, Y.; Takenaga, N.; Kita, Y. First hypervalent iodine(III)-catalyzed C–N bond forming reaction: Catalytic spirocyclization of amides to *N*-fused spirolactams. *Chem. Commun.* **2007**, 1224–1226. [CrossRef] [PubMed]
20. Yakura, T.; Yamauchi, Y.; Tian, Y.; Omoto, M. Catalytic Hypervalent Iodine Oxidation of *p*-Dialkoxybenzenes to *p*-Quinones Using 4-Iodophenoxyacetic Acid and Oxone®. *Chem. Pharm. Bull.* **2008**, *56*, 1632–1634. [CrossRef] [PubMed]
21. Matsumoto, R.; Nishino, H. Advanced Synthesis of Dihydrofurans. Effect of Formic Acid on the Mn(III)-Based Oxidation. *Synth. Commun.* **2015**, *45*, 1807–1816. [CrossRef]
22. Heiba, E.I.; Dessau, R.M.; Koehl, W.J., Jr. Oxidation by Metal Salts. III. The Reaction of Manganic Acetate with Aromatic Hydrocarbons and the Reactivity of the Carboxymethyl Radical. *J. Am. Chem. Soc.* **1969**, *91*, 138–145. [CrossRef]
23. Nishino, H.; Kurosawa, K. Regioselective Carboxylation of 9-Xanthenones with Manganese(III) Acetate. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 474–480. [CrossRef]
24. Nishino, H.; Kamachi, H.; Baba, H.; Kurosawa, K. Manganese(III)-Mediated Carbon-Carbon Bond Formation in the Reaction of Xanthenes with Active Methylene Compounds. *J. Org. Chem.* **1992**, *57*, 3551–3557. [CrossRef]
25. Nishino, H. Manganese(III)-Based Peroxidation of Alkenes to Heterocycles. In *Bioactive Heterocycles I*; Topics in Heterocyclic Chemistry; Eguchi, S., Ed.; Springer: Berlin, Germony, 2006; pp. 39–76.
26. Rahman, M.T.; Haque, M.A.; Igarashi, H.; Nishino, H. Mn(III)-Initiated Facile Oxygenation of Heterocyclic 1,3-Dicarbonyl Compounds. *Molecules* **2011**, *16*, 9562–9581. [CrossRef] [PubMed]
27. Ju, Y.; Miao, D.; Seo, J.G.; Koo, S. Catalytic Oxidation of β-Keto Esters by Manganese(III)/Cobalt(II) and Consecutive Cyclization to Heterocycles. *Adv. Synth. Cat.* **2014**, *356*, 3059–3066. [CrossRef]
28. Nguyen, V.-H.; Nishino, H.; Kurosawa, K. Manganese(III)-Based Facile Synthesis of 3-Cyano-4,5-dihydrofurans and 4-Cyano-1,2-dioxan-3-ols Using Alkenes and Acylacetonitrile Building Blocks. *Synthesis* **1997**, 899–908. [CrossRef]
29. Bhattacharjee, M.N.; Chaudhuri, M.K.; Khathing, D.T. Direct Synthesis of Tris(acetylacetonato)manganese(III). *J. Chem. Soc. Dalton Trans.* **1982**, 669–670. [CrossRef]
30. Shi, L.-X.; Zhang, V.W.; Wu, C.-D. The synergistic effect of $[WZn(VO)_2(ZnW_9O_{34})_2]^{12-}$ cores and peripheral metal sites in catalytic oxidative cyclization of acetylacetone. *Dalton Trans.* **2011**, *40*, 779–781. [CrossRef] [PubMed]
31. Kikue, N.; Takahashi, T.; Nishino, H. Mn(III)-Based Oxidative Cyclization of *N*-Aryl-3-oxobutanamides. Facile Synthesis and Transformation of Substituted Oxindoles. *Heterocycles* **2015**, *90*, 540–562.
32. Kozminykh, E.N.; Goncharov, V.I.; Oborin, D.B.; Kozminykh, V.O. A Simple Method for the Synthesis of Esters of 2-Hydroxy-3-oxo-2,3-dihydrofuran-2-ylacetic Acid. *Chem. Heterocycl. Com.* **2007**, *43*, 658–656. [CrossRef]