Oxidation of 2,5-Dimethoxyacetophenone Derivatives with Thallium(III) Nitrate in Trimethyl Orthoformate-Methanol. I

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Alkyl-substituted 2,5-dimethoxyacetophenones were oxidized with thallium(III) nitrate in methanol–trimethyl orthoformate (TMOF) to give methyl alkyl-substituted 2,5-dimethoxyphenylacetates in a good yield. A simple modification of separating method from the reacting mixture allowed us to obtain the corresponding methyl (alkyl-substituted 3,6-dioxo-1,4-cyclohexadienyl)acetates.

Oxidations of alkyl-substituted 2,5-dimethoxyacetophenones **1** with thallium(III) nitrate were investigated. Using an acidified methanol with perchloric acid as the solvent, we obtained methyl esters of alkyl-substituted-3,6-dioxo-1,4-cyclohexadienylacetic acids **4** by the oxidation in a high yield. By the oxidation we expected to have methyl esters of alkyl-substituted 2,5-dimethoxyphenylacetic acids **2**, but every effort to yield **2** ended without success. However, changing the solvent from MeOH–$HClO_4$ to absolute MeOH–trimethyl orthoformate (TMOF), we obtained **2** in excellent yields at last. In this paper the oxidation method will be described in detail.

Results and Discussion

Alkyl-substituted 2,5-dimethoxyacetophenones **1** dissolved in absolute MeOH–TMOF were oxidized with thallium(III) nitrate trihydrate at 0 °C. After approximately 10 min the oxidation was completed, and the resulting mixture was passed through a short column filled with basic alumina. Then, evaporation of the solvent gave us an excellent yield of methyl esters of alkyl-substituted 2,5-dimethoxyphenylacetic acids **2**. However, if we save the basic alumina treatment other products will be obtained; that is, **4**, oxidation product of **2**, instead of **2**. Recently, use of $Tl(NO_3)_3 \cdot 3H_2O$ in MeOH–TMOF, or anhydrous $Tl(NO_3)_3$ on solid support has been reported to allow a high conversion of acetophenones to the corresponding methyl esters of α-methoxyphenylacetic acids, $C_6H_5CH(OMe)CO_2Me$.[1,2]

On the contrast, the present work showed that oxidation of **1** with $Tl(NO_3)_3 \cdot 3H_2O$ in absolute MeOH–TMOF gave an excellent yield of **2** together with only a small amount of the corresponding α-methoxylated phenylacetates **3**. Thus, by our procedure **2** was obtained predominantly. If we saved the basic alumina treatment, **4** was the major product. The results of representative reactions are summarized in Table 1.

Oxidation of 2,5-dimethoxy-4-methylpropiophenone **6** with $Tl(NO_3)_3 \cdot 3H_2O$ in MeOH–TMOF gave a quantitative yield of methyl ester of 2-(2,5-dimethoxy-4-methylphenyl)propionic acid **7**, although the oxidation of **6** in MeOH–$HClO_4$ scarcely gave **7** or its oxidized product; methyl ester of 2-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)propionic acid **8**. Without the basic alumina treatment we obtained **8** as the single product (96%). 2,4,5-Trimethoxyacetophenone **1g** is also smoothly oxidized to yield methyl ester of 2,4,5-trimethoxyphenylacetic acid **2g**. Without basic alumina treatment we obtained a complex mixture composed of intractable substances.

Concerned to the oxidation of acetophenone in MeOH–TMOF, Taylor *et al.* have reported a smooth production of methyl ester of α-methoxyphenylacetic acid. However, they did not obtained any methyl ester of phenylacetic acid, and excluded the possible intermediacy of it in the oxidation. As the evidence they gave the fact that methyl phenylacetate was recovered unchanged in the oxidation with $Tl(NO_3)_3 \cdot 3H_2O$ in MeOH–TMOF. In spite of the Taylor's work, our investigation indicates a possible intermediacy of methyl ester of alkyl-substituted 2,5-dimethoxyphenylacetic acid **2**. Table 2 shows clearly the gradual change of **2b** to **3b** on standing the reacting mixture. The discrepancy between Taylor's work and ours might be due to the absence and presence of NO_3^-, HCO_2CH_3, and thallium(I) nitrate in the reacting mixture. As the oxidation proceeds, these three species can be produced in the reacting mixture. Taylor's blank test was performed in

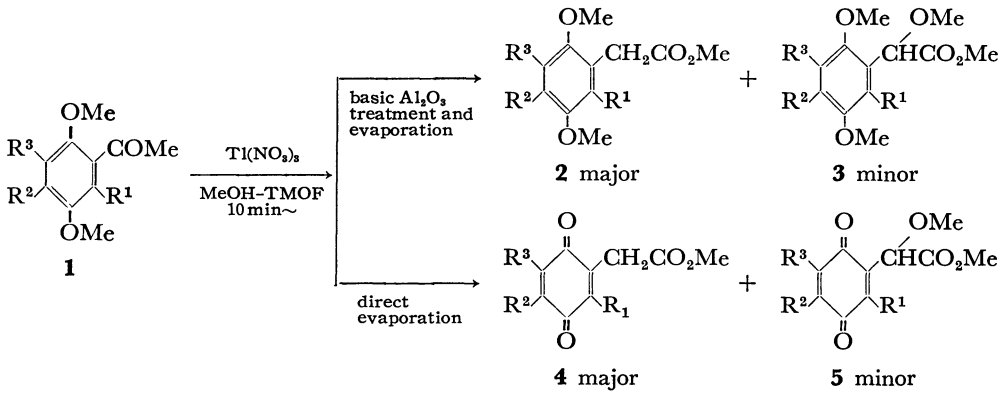
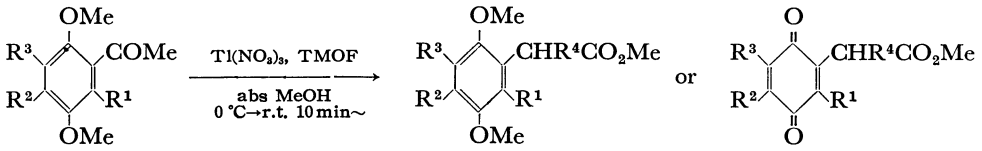


Table 1.



1

2 R^4=H
3 R^4=OMe

4 R^4=H
5 R^4=OMe

Compound	R^1	R^2	R^3	Yield[a] (%) of **2**+**3**	**2**: **3**[d]	Yield[b] (%) of **4**+**5**	**4**: **5**[d]
1a	H	H	H	84	85: 15	— (85)[c]	
1b	H	Me	H	90	90: 10	93	84: 16
1c	H	*t*-Bu	H	93	85: 15	95	88: 12
1d	H	Me	Me	96	80: 20	52	90: 10
1e	Me	Me	H	80	92: 8	47	70: 30
1f	H	CH=CH–CH=CH		84	81: 19	35	80: 20
1g	H	OMe	H	98	93: 7	—	—

a) Isolation of **2** and **3**: with Al_2O_3 treatment (work-up method A). b) Isolation of **4** and **5**: without Al_2O_3 treatment (work-up method B). c) No **4a** and **5a** were isolated, the yield of methyl 2,5-dimethoxy-4-nitrophenylacetate is given. d) The ratio of isomers (**2**/**3** and **4**/**5**) in both cases was determined by comparison of GLPC area ratios and/or integration of NMR signals.

Table 2. Oxidative rearrangement of **1b** to **2b**, **3b**

Reaction time (h)	**2b**/**3b**[a]	Isolated yield (%)	
		2b	**3b**
0.25[b]	90/10	81	9
1	85/15	—	—
3	83/17	—	—
24	13/87	9	61

a) The relative product ratio **2b**/**3b** were determined by GLPC analysis. b) At that time the oxidation was completed.

the absence of the above species in the reacting mixture.

Experimental

Melting points were taken on a Yanagimoto micro-melting apparatus and are uncorrected. ^{1}H NMR spectra were recorded in deuteriochloroform solutions with a JEOL PS-100 instrument using tetramethylsilane as an internal standard. IR spectra were measured with a JASCO IR-S spectrometer in KBr disk or liquid film techniques. Mass spectra were determined on a Hitachi M-52 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory of Kyoto University. GLPC analyses were performed using JEOL JGC-20K gas chromatographs equipped with a 2 m silicon SE-30 (5%) column. The analyses were reconfirmed with the use of another column; *i.e.*, 1 m silicon DC-550 (10%). Column chromatography was performed over basic alumina, silica gel (Wako Pure Chem. Ind.) and Florisil 100—200 mesh (Floridin Com., U.S.A). The ratio of isomeric products (**2**/**3** and **4**/**5**) was determined by integration of GLPC signals, and/or of the NMR signals (see Tables 1 and 2).

Starting Materials. All of the compounds **1a**—**g** were prepared by the Friedel-Crafts acylation of the corresponding hydroquinone dimethyl ethers with acetyl chloride in the presence of titanium tetrachloride in carbon disulfide. 2,5-Dimethoxy-4-methylpropiophenone **6** was prepared by the similar methods. All were purified by either distillation or recrystallization. 2,5-Dimethoxyacetophenone **1a**, bp 114—116 °C/5 mmHg (lit,[3] bp 156—158 °C/15 mmHg), 2,5-dimethoxy-4-methylacetophenone **1b**, mp 73—75 °C, 4-*t*-butyl-2,5-dimethoxyacetophenone **1c**, mp 64—65 °C, 2,5-dimethoxy-3,4-dimethylacetophenone **1d**, bp 123—130 °C/3 mmHg, 3,6-dimethoxy-2,4-dimethylacetophenone **1e**, bp 123—125 °C/3 mmHg, 2-acetyl-1,4-dimethoxynaphthalene **1f**, mp 59—60.5 °C, 2,4,5-trimethoxyacetophenone **1g**, mp 102 °C, 2,5-dimethoxy-4-methylpropiophenone **6**, mp 78 °C.

General Procedure for the Oxidation of 2,5-Dimethoxyacetophenones. To a solution of TMOF (1 ml) and $Tl(NO_3)_3 \cdot 3H_2O$ (1 g) in abs methanol (5 ml) 2,5-dimethoxyacetophenone **1** (2 mmol) was added at once with stirring at 0 °C, and then the resulting mixture was allowed to stand at room temperature for 5 min. The reaction was continued till the white precipitates of thallium(I) nitrate crystallized out. After filtration of thallium(I) nitrate the filtrate was worked up in the following two methods; A and B. Work-up method A: the filtrate was diluted with petroleum ether (50 ml), and passed through a short column of basic alumina (20 g) by eluting with dichloromethane (200 ml). Evaporation of dichloromethane gave a mixture of **2** and **3**. Work-up method B: the filtrate was concentrated directly *in vacuo* (<40 °C). The residure was passed through a short column of Florisil (20 g) using dichloromethane (200 ml) as an eluent. Evaporation of dichloromethane gave a mixture of **4** and **5**. The analytical samples **2** and **3** were separated by preparative GLPC. The pure product **4** was isolated by chromatography on silica gel using benzene or dichloromethane as an eluent.

Methyl 2,5-Dimethoxyphenylacetate ***2a*** *and Methyl α,2,5-Trimethoxyphenylacetate* ***3a***. Followed to the work-up method A oxidation of **1a** with $Tl(NO_3)_3$–TMOF–MeOH (reaction time: 15 min) gave a mixture of products **2a** and **3a** (**2a**: **3a**=85: 15) in 84% yield. Compound **2a**, mp 46—47 °C; MS, *m/e*, 210; IR(KBr) 1742 cm^{-1}; NMR($CDCl_3$) δ=3.59 (s, 2H, CH_2), 3.67 (s, 3H, CO_2CH_3), 3.73 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.75 (s, 3H, ArH); Found: C, 63.08; H, 6.75%. Calcd for $C_{11}H_{14}O_4$: C, 62.84, H, 6.71%. Compound **3a**, oil; MS, *m/e*, 240; IR(NaCl) 1752 cm^{-1}; NMR ($CDCl_3$) δ=3.40 (s, 3H, OCH_3), 3.71 (s, 3H, CO_2CH_3), 3.76 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 5.17 (s, 1H, CH), 6.82, 6.84, and 6.95 (m, 3H, ArH); Found: C, 59.73; H, 6.92%. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71%.

Methyl 2,5-Dimethoxy-4-methylphenylacetate ***2b*** *and Methyl α,2,5-Trimethoxy-4-methylphenylacetate* ***3b***. Oxidation of **1b** with $Tl(NO_3)_3$–TMOF–MeOH (reaction time: 15 min) applied

with the work-up method A gave a mixture of products **2b** and **3b** (**2b**: **3b**=90: 10) in 90% yield. Compound **2b**, mp 69—70 °C; MS; *m/e*, 224; IR(KBr) 1735 cm^{-1}; NMR($CDCl_3$) δ=2.26 (s, 3H, CH_3), 3.63 (s, 2H, CH_2), 3.72 (s, 3H, CO_2CH_3), 3.79 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.71 (s, 2H, ArH); Found: C, 64.32; H, 7.06%. Calcd for $C_{13}H_{18}O_5$: C, 64.27; H, 7.14%. Compound **3b**, mp 70—71 °C; MS, *m/e*, 254; IR(KBr) 1750 cm^{-1}; NMR($CDCl_3$) δ=2.23 (s, 3H, CH_3), 3.38 (s, 3H, OCH_3), 3.71 (s, 3H, CO_2CH_3), 3.78 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.20 (s, 1H, CH), 6.74 (s, 1H, ArH), 6.85 (s, 1H, ArH); Found: C, 61.29; H, 7.25%. Calcd for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14%.

Methyl 4-t-Butyl-2,5-dimethoxyphenylacetate ***2c*** *and Methyl α,2,5-Trimethoxyphenylacetate* ***3c***. Oxidation of **1c** with $Tl(NO_3)_3$–TMOF–MeOH for 30 min resulted a reacting mixture. Immediate application of the work-up method A gave a mixture of products **2c** and **3c** (**2c**: **3c**=85: 15) in 93% yield. Compound **2c**, mp 52.5—54.5 °C; MS, *m/e*, 266; IR(KBr) 1741 cm^{-1}; NMR ($CDCl_3$) δ=1.36 (s, 9H, *t*-Bu), 3.57 (s, 2H, CH_2), 3.67 (s, 3H, CO_2CH_3), 3.76 (s, 6H,OCH_3), 6.70 (s, 1H, ArH), 6.81 (s, 1H, ArH); Found: C, 67.47; H, 8.37%. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33%. Compound **3c**, mp 46.5—47 °C, MS, *m/e*, 296; IR(KBr) 1760 cm^{-1}; NMR ($CDCl_3$) δ=1.36 (s, 9H, *t*-Bu), 3.38 (s, 3H, OCH_3), 3.71 (s, 3H, CO_2CH_3), 3.77 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 5.17 (s, 1H, CH), 6.84 (s, 1H, ArH); Found: C, 64.74; H, 8.29%. Calcd for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16%.

Methyl 2,5-Dimethoxy-3,4-dimethylphenylacetate ***2d*** *and Methyl α,2,5-Trimethoxy-3,4-dimethylphenylacetate* ***3d***. Oxidation of **1d** with $Tl(NO_3)_3$–TMOF–MeOH for 30 min resulted a reacting mixture. Subsequent application of the work-up method A gave a mixture of products **2d** and **3d** (**2d**: **3d**= 80: 20) in 96% yield. Compound **2d**, oil; MS, *m/e*, 238; IR(NaCl) 1740 cm^{-1}; NMR ($CDCl_3$), δ=2.12 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.63 (s, 2H, CH_2), 3.65 (s, 3H, CO_2CH_3), 3.70 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.60 (s, 1H, ArH); Found: C, 65.33; H, 7.67%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%. Compound **3d**, oil; MS, *m/e*, 268; IR(NaCl) 1750 cm^{-1}; NMR ($CDCl_3$) δ=2.13 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.38 (s, 3H, OCH_3), 3.73 (s, 3H, CO_2CH_3), 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 5.15 (s, 1H, CH), 6.72 (s, 1H, ArH); Found: C, 62.66; H, 7.54%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

Methyl 3,6-Dimethoxy-2,4-dimethylphenylacetate ***2e*** *and Methyl α,3,6-Trimethoxy-2,4-dimethylphenylacetate* ***3e***. Oxidation of **1e** with $Tl(NO_3)_3$–TMOF–MeOH for 20 h application of the work-up method A gave a mixture of products **2e** and **3e** (**2e**: **3e**=92: 8) in 80% yield. Compound **2e**, mp 50—52 °C; MS, *m/e*, 238; IR(KBr) 1732 cm^{-1}; NMR ($CDCl_3$) δ=2.20 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.64 (s, 2H, CH_2), 3.67 (s, 3H, CO_2CH_3), 3.67 (s, 3H, OCH_3), 3.76 (s, 3H, CH_3), 6.56 (s, 1H, ArH); Found: C, 65.49; H, 7.57%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%. Compound **3e**, oil, MS, *m/e*, 268; IR(NaCl) 1745 cm^{-1}; NMR ($CDCl_3$) δ=2.25 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.39 (s, 3H, OCH_3), 3.65 (s, 3H, CO_2CH_3), 3.72 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.31 (s, 1H, CH), 6.59 (s, 1H, ArH); Found: C, 62.56; H, 7.59%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

Methyl (1,4-Dimethoxy-2-naphthyl)acetate ***2f*** *and Methyl α-Methoxy-α-(1,4-dimethoxy-2-naphthyl)acetate* ***3f***. Oxidation of **1f** with $Tl(NO_3)_3$–TMOF–MeOH for 5 h resulted a reacting mixture. Applying the work-up method A we obtained a mixture of products **2f** and **3f** (**2f**: **3f**=81: 19) in 84% yield. Compound **2f**, oil; MS, *m/e*, 260; IR(NaCl) 1730 cm^{-1}; NMR ($CDCl_3$) δ=3.71 (s, 3H, CO_2CH_3), 3.82 (s, 2H, CH_2), 3.88 (s. 3H, OCH_3), 3.96 (s, 3H, OCH_3), 6.65 (s, 1H, ArH), 7.47 (m, 2H, ArH), 8.00 (m, 1H, ArH), 8.19 (m, 1H, ArH); Found: C, 69.18; H, 6.35%. Calcd for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20%. Compound **3f**, oil, MS, *m/e*, 290; IR(NaCl) 1750 cm^{-1}; NMR ($CDCl_3$) δ=3.41 (s, 3H, OCH_3), 3.73 (s, 3H, CO_3CH_3), 3.97 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 5.41 (s, 1H, CH), 6.77 (s, 1H, ArH), 7.51 (m, 2H, ArH), 8.04 (m, 1H, ArH), 8.21 (m, 1H, ArH); Found: C, 66.70; H, 6.14%. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25%.

Methyl 2,4,5-Trimethoxyphenylacetate ***2g*** *and Methyl α,2,4,5-Tetramethoxyphenylacetate* ***3g***. Oxidation of **1g** with $Tl(NO_3)_3$–TMOF–MeOH for 30 min gave a reacting mixture. After treating it with work-up method A a mixture of products **2g** and **3g** (**2g**: **3g**=93: 7) was obtained in 98% yield. Compound **2g**, mp 44—46 °C; MS, *m/e*, 240; IR(KBr) 1735 cm^{-1}; NMR ($CDCl_3$) δ=3.56 (s, 2H, CH_2), 3.67 (s, 3H, CO_2CH_3), 3.78 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.49 (s, 1H, ArH), 6.70 (s, 1H, ArH); Found: C, 59.99; H, 6.75%. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71%. Compound **3g**, mp 47—49 °C, MS, *m/e*, 270; IR(KBr) 1758 cm^{-1}; NMR ($CDCl_3$) δ=3.37 (s, 3H, OCH_3), 3.72 (s, 3H, CO_2CH_3), 3.84 (s, 6H, $OCH_3\times2$), 3.89 (s, 3H, OCH_3), 5.19 (s, 1H. CH). 6.52 (s, 1H, ArH), 6.91 (s, 1H, ArH); Found: C, 57.77; H, 6.77%. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71%.

Methyl 2,5-Dimethoxy-4-nitrophenylacetate. Treatment of **1a** with $Tl(NO_3)_3$–TMOF–MeOH for 15 min according to the general procedure, followed by work-up method B, gave the methyl 2,5-dimethoxy-4-nitrophenylacetate in 85% yield: mp 80—81 °C; MS, *m/e*, 255; IR(KBr) 1735 and 1519 cm^{-1}; NMR ($CDCl_3$) δ=3.66 (s, 2H, CH_2), 3.69 (s, 3H, CO_2CH_3), 3.83 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 6.94 (s, 1H, ArH), 7.35 (s, 1H, ArH); Found: C, 51.76; H, 5.17; N, 5.43%. Calcd for $C_{11}H_{13}O_6N$: C, 51.76; H, 5.13; N, 5.49%.

Methyl 4-Methyl-3,6-dioxo-1,4-cyclohexadienylacetate ***4b***. Oxidation of **1b** with $Tl(NO_3)_3$–TMOF–MeOH for 15 min according to the general procedure, followed by work-up method B, gave a mixture of products **4b** and **5b** (**4d**: **5b**= 84: 16) in 93% yield. Compound **4b**, mp 74—75 °C; MS, *m/e*, 194; IR(KBr) 1730 and 1675 cm^{-1}; NMR ($CDCl_3$) δ=2.03 (d, J=1.6 Hz, 3H, CH_3), 3.42 (d, J=1.2 Hz, 2H, CH_2), 3.69 (s, 3H, CO_2CH_3), 6.60 (q, J=1.6 Hz, 1H, =CH), 6.65 (t, J=1.2 Hz, 1H, =CH); Found: C, 61.60; H, 5.12%. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%.

Methyl 4-t-Butyl-3,6-dioxo-1,4-cyclohexadienylacetate ***4c***. Oxidation of **1c** with $Tl(NO_3)_3$–TMOF–MeOH for 30 min according to the general procedure resulted a reacting mixture. Subsequent application of the work-up method B we obtained a mixture of products **4c** and **5c** (**4c**: **5c**=88: 12) in 95% yield. Isolation of the product **4c** was carried out as described above and gave oil; MS, *m/e*, 208; IR(NaCl) 1735 and 1670 cm^{-1}; NMR ($CDCl_3$) δ=2.02 (s, 6H, $CH_3\times2$), 3.45 (d, J=1.2 Hz, CH_2), 3.72 (s, 3H, CO_2CH_3), 6.67 (t, J=1.2 Hz, 1H, =CH); Found: C, 63.71; H, 5.99%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Methyl 4,5-Dimethyl-3,6-dioxo-1,4-cyclohexadienylacetate ***4d***. Oxidation of **1d** with $Tl(NO_3)_3$–TMOF–MeOH for 30 min according to the general procedure, follwed by work-up method B, gave a mixture of products **4d** and **5d** (**4d**: **5d**= 90: 10) in 52% yield. Compound **4d**, oil; MS, *m/e*, 208; IR(NaCl) 1735 and 1670 cm^{-1}; NMR ($CDCl_3$) δ=2.02 (s, 6H, $CH_3\times2$), 3.45 (d, J=1.2 Hz, 2H, CH_2), 3.72 (s, 3H, CO_2CH_3), 6.67 (t, J=1.2 Hz, 1H, =CH); Found: C, 63.71; H, 5.99%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Methyl 2,4-Dimethyl-3,6-dioxo-1,4-cyclohexadienylacetate ***4e***. Oxidation of **1e** with $Tl(NO_3)_3$–TMOF–MeOH for 20 h according to the general procedure resulted a reacting mixture. Applying the work-up method B we obtained a mixture of products **4e** and **5e** (**4e**: **5e**=70: 30) in 47% yield. Compound **4e**, oil; MS, *m/e*, 208; IR(NaCl) 1740 and 1652 cm^{-1}; NMR

($CDCl_3$) δ=2.05 (d, J=1.6 Hz, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.54 (s, 2H, CH_2), 3.68 (s, 3H, CO_2CH_3), 6.56 (q, J=1.6 Hz, 1H, =CH), Found: C, 63.79; H, 6.02%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

Methyl 1,4-Dioxo-1,4-dihydro-2-naphthylacetate ***4f***. Oxidation of **1f** with $Tl(NO_3)_3$–TMOF–MeOH for 5 h according to the general procedure application of the work-up method B gave a mixture of products **4f** and **5f** (**4f**: **5f**=80: 20) in 35% yield. Compound **4f**, mp 123—125 °C; MS, *m/e*, 230; IR(KBr) 1735 and 1665 cm^{-1}; NMR ($CDCl_3$) δ=3.58 (d, J=1.5 Hz, 1H, CH_2), 3.72 (s, 3H, CO_2CH_3), 6.91 (t, J=1.5 Hz, 1H, =CH), 7.70 (m, 2H, ArH), 8.04 (m, 2H, ArH); Found: C, 67.55; H, 4.20%. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38%.

Methyl 2-(2,5-Dimethoxy-4-methylphenyl)propionate ***7***. Oxidation of **6** with $Tl(NO_3)_3$–TMOF–MeOH for 12 h gave a reacting mixture. Treatment of it with the work-up method A afforded a pure product **7** in 92% yield. Compound **7**, oil. MS, *m/e*, 238; IR(NaCl) 1735 cm^{-1}; NMR ($CDCl_3$) δ=1.42 (d, J=7 Hz, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.64 (s, 3H, CO_2CH_3), 3.77 (s, 6H, $OCH_3\times2$), 4.03 (q, J=7 Hz, 1H, CH), 6.70 (s, 2H, ArH); Found: C, 65.39; H, 7.65%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%.

Methyl 2-(4-Methyl-3,6-dioxo-1,4-cyclohexadienyl)propionate ***8***. Treatment of **6** with $Tl(NO_3)_3$–TMOF–MeOH for 12 h according to the general procedure, followed by work-up method B, gave a pure product **8** in 96% yield. Compound **8**, mp 59—60 °C; MS, *m/e*, 208; IR(KBr) 1735 and 1655 cm^{-1}; NMR ($CDCl_3$) δ=1.41 (d, J=7.2 Hz, 3H, CH_3), 2.08 (d, J=1.6 Hz, 3H, CH_3), 3.70 (s, 3H, CO_2CH_3), 3.79 (dq, J=7.2 Hz, J=1.2 Hz, 1H, CH), 6.60 (m, 2H, $=CH\times2$); Found: C, 63.27; H, 6.11%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

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