Oxidative Decarboxylation of Arylacetic Acids with Manganese(III) Acetate

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The oxidative decarboxylation reactions of arylacetic acids to arylcarbinols were compared for Mn(III) acetate, Ce(IV) ammonium nitrate and a combination reagent of Co(III) acetate–Cu(II) acetate. The reaction with Mn(III) acetate in acetic acid gave the corresponding arylcarbinyl acetate usually in good yield. The reaction was particularly easy when the substrate carried an electron-donating group at the *para* position of the aromatic ring, or when the acid was secondary or tertiary. In contrast, the product generated with the other reagents was either a mixture containing over-oxidation products or products formed *via* a different route.

Key words oxidative decarboxylation; arylacetic acid; Mn(III) acetate; electron donating group; Ce(IV) ammonium nitrate; Co(III) acetate–Cu(II) acetate

Arylacetic acids, particularly those whose carboxylic acid is secondary or tertiary, when irradiated in alkaline media, smoothly give arylalkanes as decarboxylation products.[1] When this process is accompanied with the introduction of an oxygenated function such as an acyloxy group or dehydrogenation, the products will be arylmethylcarbinols or arylalkenes. Such oxidative decarboxylation has been achieved by using Pb(IV) acetate or Ag(II) oxide,[2] but their use is limited because of their high oxidative power.[3] A combination of Co(III) acetate and Cu(II) acetate was recently proposed as a safe and suitable reagent.[4]

In this paper, we show that Mn(III) acetate is superior to that reagent for this purpose. It has previously been used for auto-oxidation of aromatic compounds[5] and also for oxidative decarboxylation of aliphatic carboxylic acids,[6] but has not been applied to arylacetic acids except for a few examples by Finkbeiner *et al.*[5] Although similar results are expected to be obtainable by Ce(IV) ammonium nitrate (CAN) oxidation, since CAN has been used for the introduction of an oxygenated function at a benzylic position,[7] we hoped that Mn(III) would be more selective than Ce(IV), because its oxidation–reduction potential is smaller than that of Ce(IV).[8] Thus, the result of CAN oxidation was also compared with that of Mn(III) oxidation.

Results and Discussion

Firstly, the oxidation of five primary arylacetic acids **1a**—**e** with $Mn(OAc)_3$ in AcOH was examined. As can be seen in Table 1, those which carry an electron-releasing group at the *para* position (**1b**, **1d**, **1e**) smoothly gave the benzylacetates **2b**, **2d**, and **2e** in high yields, whereas the oxidation of **1a** and **1c**, which do not possess such an activating group, required a longer reaction time, and the yields of the corresponding acetates **2a** and **2c** were lower. By-products in this oxidation were the arylaldehydes **3**, which were produced by over-oxidation. 4-Methylphenylacetic acid (**1f**) also gave 4-methylbenzyl acetate (**2f**) with an intact methyl group in 65% yield, together with 20% recovery of the starting material (**1f**).

Oxidation of **1b** with a $Co(OAc)_3$–$Cu(OAc)_2$ combination[4] gave **2b** and the over-oxidation product **3b** in 85% and 15% yields, respectively. On the other hand, oxidation of **1a**—**f** with CAN in MeCN–AcOH gave a complicated result. The products were mixtures of **2**, **3**, **5**, and **6**. The major product for **1a**, **1b**, and **1f** was the nitrate **5**, and the formation of the Ritter-type product **6** was sometimes observed (entries 2, 5). The latter compound **6** was also observed in the Mn(III) oxidation, though the yield was low, when the reaction was carried out in AcOH–MeCN, suggesting that benzyl cation was formed in the reaction. The 3,4-dimethoxy derivative (**1d**), on CAN oxidation, gave the benzyl acetate (**2d**) in very low yield together with the over-oxidation product (**3d**, 16%) and the nitro derivative (**7d**). The 3,4-methylenedioxy derivative (**1e**) gave poor results in CAN oxidation (entry 12), suggesting that the reaction proceeded in a completely different manner: for example, introduction of OAc into the methylenedioxy group.[9]

4-Fluoro-, 4-chloro-, and 4-bromophenylacetic acids (**1h**—**j**) gave results similar to those in the oxidation of **1a**, except that they gave the diacetate (**7**) as a by-product with an appreciable recovery of the starting material. 4-Nitrophenylacetic acid (**1g**) was also oxidized by $Mn(OAc)_3$ with a comparable speed to that of **1a**, but gave 4-nitrobenzaldehyde (**3g**) as a major product together with its diacetate (**7g**), instead of **2g**. CAN also gave a comparable result (entry 16).

Although oxidation of aromatic compounds with Mn(III) in AcOH gave rather complicated results,[5] oxidative decarboxylation of arylacetic acids seems to proceed in a simpler manner, possibly *via* the route depicted in Chart 1. Over-oxidation may proceed through a repetition of the process involved in the formation of benzyl acetates (**2**), where introduction of the second OAc group is controlled by the electonic nature of the *p*-substituent. Failure to isolate **2g** or the starting material from the oxidation of **1g** is rather curious, and may suggest instability of the nitro group to Mn(III) oxidation. Speculatively, a Mn(II) species formed in this reaction may participate in the reduction of the nitro group.

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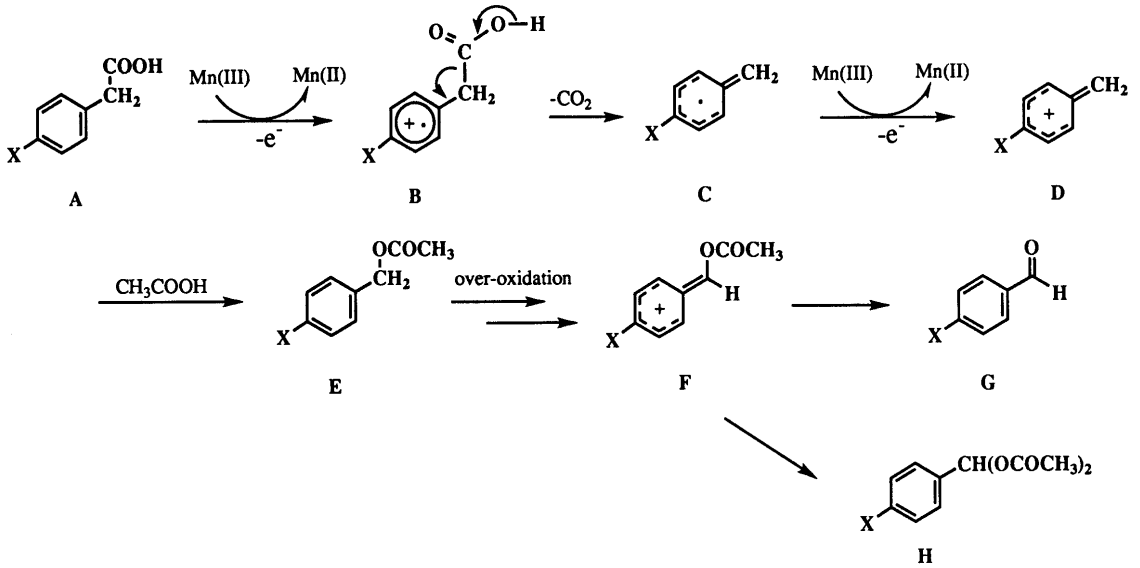
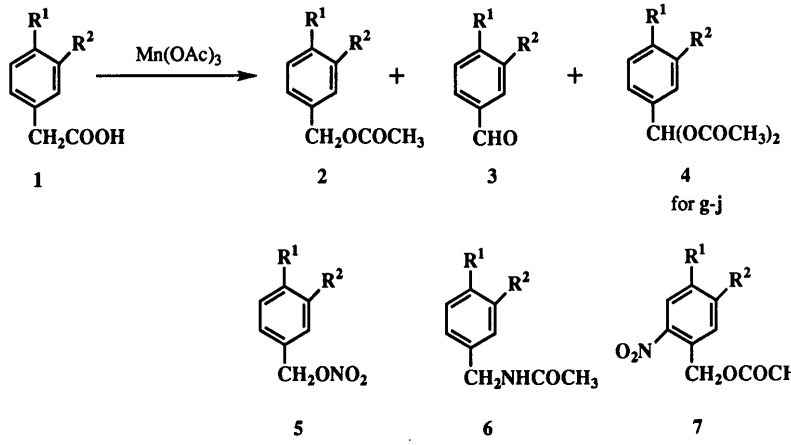


Chart 1



a : R^1=R^2=H, **b** : R^1=OCH_3, R^2=H, **c** : R^1=H, R^2=OCH_3, **d** : R^1=R^2=OCH_3, **e** : R^1,R^2=OCH_2O,

f : R^1=CH_3, R^2=H, **g** : R^1=NO_2, R^2=H, **h** : R^1=F, R^2=H, **i** : R^1=Cl, R^2=H, **j** : R^1=Br, R^2=H

Chart 2

Next, oxidative decarboxylation of secondary arylacetic acids was examined, taking 2-(4′-methoxyphenyl)propionic acid (**8**) as a model compound. $Mn(OAc)_3$ gave the expected acetate (**9**) in 67% yield, together with the diacetate (**10**) as a by-product (5%). The formation of **10** may be understood by assuming the intermediary formation of the styrene derivative (**12**), which is known to produce **10** on similar oxidation,[10] though **12** was not isolated in the present investigation. $Co(OAc)_3$–$Cu(OAc)_2$ gave **9** in a similar yield to $Mn(OAc)_3$, but with the additional formation of the acetophenone (**11**). CAN gave an inferior result, affording **9** and **11**.

Oxidation of the tertiary arylacetic acid (**13**) was very rapid, in agreement with the observation for pivalic acid.[6] It gave the expected styrene derivative (**14**) in 48% yield on 10 min treatment with $Mn(OAc)_3$ in AcOH, with recovery of the starting material (21%). The oxidation with $Co(OAc)_3$–$Cu(OAc)_2$ was not satisfactory and gave **15** and **19** as by-products, presumably derived from **14**.

Interestingly, CAN gave a completely different result. It produced tetrahydrofuran derivatives (**16a**, **16b**) together with the nitrates (**17**, **18**) upon reaction at 0 °C for 20 min. Compounds **16a** and **16b** had the same molecular formula, $C_{20}H_{24}O_3$, and showed in the ^{1}H-NMR spectra two methyl singlets at δ 1.53 and 1.59, in addition to the two OMe singlets at δ 3.81 and 3.77. Their stereochemistry was deduced as follows. The methylene protons of **16a** appeared as multiplets at δ 1.79—2.42, while those of **16b** appeared as a single peak at δ 2.22, indicating that pseudorotation of the tetrahydrofuran ring in **16b** is easy, while that in **16a** is difficult; the results suggest twist and envelope conformations for **16b** and **16a**, respectively. Thus, **16a** and **16b** have *cis* (*meso*) and *trans* (*dl*) stereochemistries, as depicted in Chart 4, respectively. We consider that these compounds are produced by the dimerization of the initially formed styrene derivative (**14**) followed by hydration and cyclization (see Chart 5). In fact, CAN oxidation of **14** gave compounds **16a** and **16b**. The difference of CAN oxidation from the others can presumably be ascribed to its higher oxidation power.

In conclusion, $Mn(OAc)_3$ seems to be the reagent of choice for oxidative decarboxylation of arylacetic acids.

Table 1. Oxidation of Arylacetic Acids **1**

Entry	Arylacetic acid 1			Conditions				Yield (%)[a] of						
	R^1	R^2		Oxidant (eq)[b]	Solvent	Temp.	Time	**2**[12]	**3**[13]	**4**[14]	**5**[15]	**6**[16]	**7**[17]	sm
1	H	H	**a**	$Mn(OAc)_3$	AcOH	Reflux	8 h	34 (48)[c]	2[d]	—	—	—	—	15
2	H	H	**a**	CAN	CH_3CN–AcOH	90 °C	6 h	9	Trace	—	48	10	—	—
3	OCH_3	H	**b**	$Mn(OAc)_3$	AcOH	Reflux	0.5 h	90	8	—	—	—	—	—
4	OCH_3	H	**b**	$Mn(OAc)_3$	CH_3CN–AcOH	90 °C	1 h	42	4	—	—	3	—	—
5	OCH_3	H	**b**	CAN	CH_3CN–AcOH	rt	20 min	36	27	—	8	2	—	—
6	OCH_3	H	**b**	$Co(OAc)_3$(2.3)–$Cu(OAc)_2$ (1)	AcOH	Reflux	15 min	85	15	—	—	—	—	—
7	H	OCH_3	**c**	$Mn(OAc)_3$	AcOH	Reflux	6 h	53	21	—	—	—	—	—
8	H	OCH_3	**c**	CAN	CH_3CN–AcOH	90 °C	1 h	2	Trace	—	81	—	—	—
9	OCH_3	OCH_3	**d**	$Mn(OAc)_3$	AcOH	Reflux	20 min	86	7	—	—	—	—	—
10	OCH_3	OCH_3	**d**	CAN	CH_3CN–AcOH	0 °C	10 min	3	16	—	—	—	3	—
11	–O–CH_2–O–		**e**	$Mn(OAc)_3$	AcOH	Reflux	0.5 h	70	Trace	—	—	—	—	7
12	–O–CH_2–O–		**e**	CAN	CH_3CN–AcOH	rt	5 min	—	2	—	—	—	5	—
13	CH_3	H	**f**	$Mn(OAc)_3$	AcOH	Reflux	3 h	65 (77)[c]	Trace	—	—	—	—	20
14	CH_3	H	**f**	CAN	CH_3CN–AcOH	90 °C	1 h	28	Trace	—	25	9	—	—
15	NO_2	H	**g**	$Mn(OAc)_3$	AcOH	Reflux	7 h	—	38	11	—	—	—	—
16	NO_2	H	**g**	CAN	CH_3CN–AcOH	90 °C	3 h	—	13	—	3	—	—	27
17	F	H	**h**	$Mn(OAc)_3$ (4)	AcOH	Reflux	8 h	44	19[d]	—	—	—	—	21
18	F	H	**h**	CAN	CH_3CN–AcOH	90 °C	6 h	19	—	—	39	17	—	—
19	Cl	H	**i**	$Mn(OAc)_3$	AcOH	Reflux	8 h	25 (–)[e]	6	2 (–)[e]	—	—	—	42
20	Cl	H	**i**	CAN	CH_3CN–AcOH	90 °C	2 h	9	—	—	56	4	—	—
21	Br	H	**j**	$Mn(OAc)_3$	AcOH	Reflux	8 h	30	15	3	—	—	—	39
22	Br	H	**j**	CAN	CH_3CN–AcOH	90 °C	2 h	7	—	—	23	3	—	—

a) Isolation yield. *b*) Unless otherwise stated, 2.3 molar eq of $Mn(OAc)_3$ or 3 molar eq of CAN was used. *c*) Parenthetical values indicate the yield (by GLC) reported by Finkbeiner *et al.*[5] *d*) Isolated as 2,4-dinitrophenylhydrazone. *e*) Yields are not indicated. rt = room temperature.

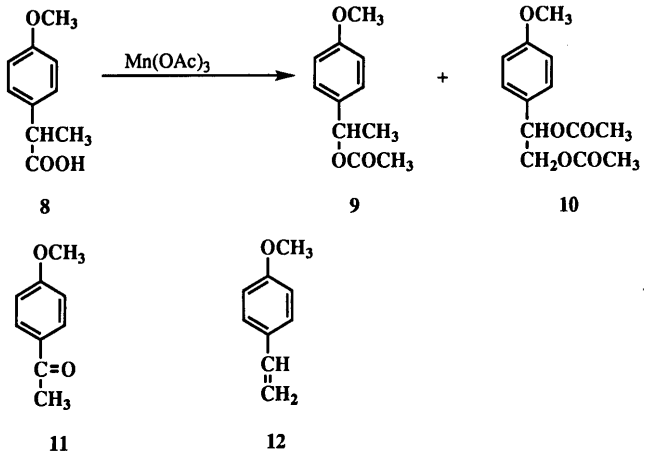


Chart 3

By reaction with this reagent in AcOH, arylacetic acids readily lose carbon dioxide, giving rise to α-acetoxylated products when they are primary or secondary and styrene derivatives when they are tertiary. Although a combination of $Co(OAc)_3$ and $Cu(OAc)_2$[4] can also be used for the same purpose, the results were inferior to those obtained with $Mn(OAc)_3$. Moreover, $Mn(OAc)_3$ is commercially available and easy to handle compared to the above combination reagent. An example of a synthetic application is shown in the reaction of **20**, which gave the cyclopentenyl derivative (**21**) in 39% yield after 10 min.

Experimental

Melting points were determined on a Yanaco micro hot stage melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR-810 spectrophotometer, and data are given in cm^{-1}. ^1H-NMR spectra were taken with a JEOL JNM-EX90 (90 MHz) spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard and the chemical shifts are given in δ values. MS and high-resolution MS (HR-MS) were taken with a JEOL JMS D-300 machine and M^+ is indicated as *m/z*. Column chromatography was carried out with Silica gel 60 (Cica-Merck). Medium-pressure liquid chromatography (MPLC) was performed on a Kusano CPS-HS-221-1 with a silica gel column (22 i.d. × 100 mm). HPLC was performed on an ODS-s-343-15 column. For TLC, Merck precoated plates GF_{254} were used and spots were monitored under UV light (254 nm), then developed by spraying 0.5% $Ce(SO_4)_2$–0.5% $(NH_4)_6Mo_7O_{24}$ in 5% H_2SO_4 and heating the plate at 100 °C until coloration took place. All organic extracts were washed with brine and dried over anhydrous sodium sulfate before concentration. Identifications of the reaction products in the case of known compounds were done by comparisons of melting points (for crystalline compounds) and spectral data (^1H-NMR, IR) with reported values.

Table 2. Oxidation of 2-(4′-Methoxyphenyl)propionic Acid **8**

Entry	Conditions				Yield (%) of		
	Oxidant (eq)	Solvent	Temp.	Time (min)	**9**[18]	**10**[19]	**11**
1	$Mn(OAc)_3$ (2.3)	AcOH	Reflux	30	67	5	—
2	$Co(OAc)_3$ (2.3)–$Cu(OAc)_2$ (1)	AcOH	Reflux	15	67	9	7
3	CAN (3)	CH_3CN–AcOH	rt	20	57	—	29

$Mn(OAc)_3$ Oxidation of Arylacetic Acids (General Procedure) A solution of an arylacetic acid (1 mmol) in AcOH (2 ml) was added to a refluxing solution of $Mn(OAc)_3 \cdot 2H_2O$ (2.3—3 eq) in AcOH (8 ml), and heating was continued for an appropriate period while monitoring the reaction by TLC. The reaction mixture was concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and insoluble Mn(II) was removed by filtration. Removal of the solvent from the filtrate and chromatography of the residue on a SiO_2 column with AcOEt–hexane gave the product, which was further separated, if necessary, by MPLC with AcOEt–hexane or by HPLC with MeOH–H_2O (3:1). See Tables 1—3.

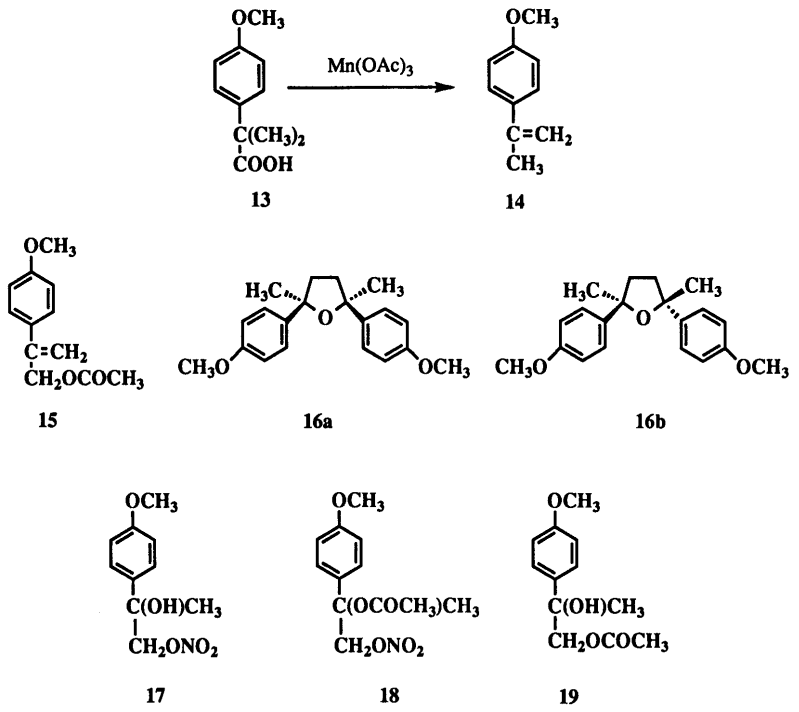


Chart 4

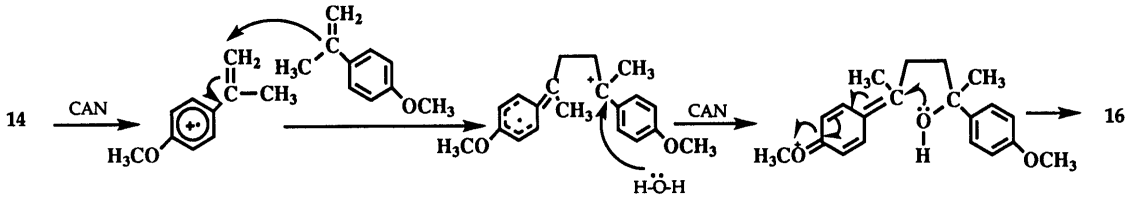


Chart 5

Table 3. Oxidation of 2-(4′-Methoxyphenyl)-2-methylpropionic Acid **13**

Entry	Conditions				Yield (%) of							
	Oxidant (eq)	Solvent	Temp.	Time (min)	**14**[20]	**15**	**16a**	**16b**	**17**	**18**	**19**[21]	sm
1	$Mn(OAc)_3$ (2.3)	AcOH	Reflux	10	48	—	—	—	—	—	—	21
2	$Co(OAc)_3$ (2.3)–$Cu(OAc)_2$ (1)	AcOH	Reflux	5	14	2	—	—	—	—	6	22
3	CAN (3)	CH_3CN–AcOH	0 °C	20	—	—	22	12	20	11	—	5

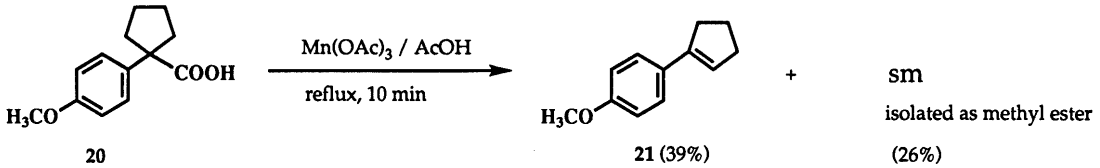


Chart 6

Oxidation of Phenylacetic Acid (1a) and 4-Fluorophenylacetic Acid (1h) The reaction mixture was concentrated under reduced pressure with a cooling trap containing dry ice. 2,4-Dinitrophenylhydrazine solution in 14% H_2SO_4 was added to the trapped mixture, and the whole was left for 10 min, then extracted with CH_2Cl_2. The organic layer was concentrated to give the 2,4-dinitrophenylhydrazone of **3a** as orange needles: mp 240—242 °C (AcOEt) and **3h** as orange prisms: mp 280—282 °C. The residue obtained on concentration of the reaction mixture was separated as described above to give **2a** and **2h**.

$Mn(OAc)_3$ Oxidation of 1a in CH_3CN–AcOH A mixture of **1a** (0.166 g, 1 mmol) in CH_3CN–AcOH (4 : 1, 2 ml) and $Mn(OAc)_3 \cdot 2H_2O$ (0.616 g, 2.3 eq) in CH_3CN–AcOH (4 : 1, 10 ml) was heated under reflux for 1 h. After work-up according to the general procedure, the product was purified by chromatography on SiO_2 and HPLC with MeOH–H_2O (3 : 1), to yield oxidation products (Table 1, entry 2).

CAN Oxidation of Arylacetic Acids (General Procedure) A solution of CAN (1.65 g, 3 eq) in CH_3CN (8 ml) was added to a solution of arylacetic acid (1 mmol) in AcOH (2 ml) and the mixture was stirred under the conditions shown in Tables 1—3. Dilution of the reaction mixture with $CHCl_3$ afforded yellow precipitates, which were removed by filtration. The filtrate was concentrated, and the residue was purified by SiO_2 column chromatography with AcOEt–hexane, and if necessary,

by MPLC with AcOEt–hexane or HPLC with MeOH–H_2O (3 : 1) to give the products (see Tables 1—3).

7d: Light yellow prisms from ether–hexane. mp 159—160 °C. IR (KBr): 1750, 1520. ^{1}H-NMR: 7.72 (1H, s, Ar-H), 7.01 (1H, s, Ar-H), 5.50 (2H, s, Ar-CH_2), 3.99 (3H, s, –OCH_3), 3.96 (3H, s, –OCH_3), 2.17 (3H, s, –$OCOCH_3$). ^{13}C-NMR: 170.4 (CO), 153.5 (C), 148.3 (C), 140.2 (C), 126.9 (C), 110.6 (CH), 108.4 (CH), 63.3 (CH_2), 56.4 (CH_3), 56.4 (CH_3), 20.9 (CH_3). LR-MS *m/z*: 255 (M^+). HR-MS: Calcd for $C_{11}H_{13}NO_6$: 255.0742. Found: 255.0682.

16a: Colorless prisms from ether. mp 156—158 °C. ^{1}H-NMR: 7.45 (4H, d, J=8.7 Hz, Ar-H), 6.87 (4H, d, J=8.7 Hz, Ar-H), 3.81 (6H, s, –OCH_3), 2.42—1.79 (4H, m, –CH_2–), 1.53 (6H, s, –CH_3). ^{13}C-NMR: 150.8 (C), 150.8 (C), 141.6 (C), 141.6 (C), 125.9 (CH), 125.9 (CH), 125.9 (CH), 125.9 (CH), 113.2 (CH), 113.2 (CH), 113.2 (CH), 113.2 (CH), 85.0 (C), 85.0 (C), 55.2 (OCH_3), 55.2 (OCH_3), 39.7 (CH_2), 39.7 (CH_2), 30.8 (CH_3), 30.8 (CH_3). LR-MS *m/z*: 312 (M^+). HR-MS: Calcd for $C_{20}H_{24}O_3$: 312.1725: Found 312.1753.

16b: Oil. ^{1}H-NMR: 7.32 (4H, d, J=8.9 Hz, Ar-H), 6.79 (4H, d, J=8.9 Hz, Ar-H), 3.77 (6H, s, –OCH_3), 2.22 (4H, s, –CH_2–), 1.59 (6H, s, –CH_3). ^{13}C-NMR: 157.9 (C), 157.9 (C), 141.1 (C), 141.1 (C), 126.2 (CH), 126.2 (CH), 126.2 (CH), 126.2 (CH), 113.3 (CH), 113.3 (CH), 113.3 (CH), 113.3 (CH), 85.1 (C), 85.1 (C), 55.2 (OCH_3), 55.2 (OCH_3), 38.8 (CH_2), 38.8 (CH_2), 32.1 (CH_3), 32.1 (CH_3). LR-MS *m/z*: 312 (M^+). HR-MS: Calcd for $C_{20}H_{24}O_3$: 312.1725. Found: 312.1737.

17: Oil. IR ($CHCl_3$): 3600, 2850, 1640, 1280. ^{1}H-NMR: 7.39 (2H, d, J=8.9 Hz, Ar-H), 6.90 (2H, d, J=8.9 Hz, Ar-H), 4.62 (1H, d, J=11.7 Hz, –CH_2), 4.48 (1H, d, J=11.7 Hz, –CH_2), 3.81 (3H, s, –OCH_3), 2.95 (1H, br s, –OH), 1.63 (3H, s, –CH_3). ^{13}C-NMR: 159.3 (C), 135.2 (C), 126.3 (CH), 126.3 (CH), 114.0 (CH), 114.0 (CH), 79.1 (CH_2), 72.8 (C), 55.3 (CH_3), 26.4 (OCH_3). LR-MS *m/z*: 227 (M^+). HR-MS: Calcd for $C_{10}H_{13}NO_5$: 227.0794. Found: 227.0795.

18: Oil. IR ($CHCl_3$): 2850, 1745, 1640, 1280. ^{1}H-NMR: 7.28 (2H, d, J=8.9 Hz, Ar-H), 6.89 (2H, d, J=8.9 Hz, Ar-H), 4.83 (1H, d, J=11.7 Hz, –CH_2), 4.55 (1H, d, J=11.7 Hz, –CH_2), 3.80 (3H, s, –OCH_3), 2.06 (3H, s, –$OCOCH_3$), 1.93 (3H, s, –CH_3). ^{13}C-NMR: 169.2 (CO), 159.4 (C), 132.0 (C), 126.2 (CH), 126.2 (CH), 114.0 (CH), 114.0 (CH), 80.7 (C), 77.4 (CH_2), 55.2 (CH_3), 22.0 (CH_3), 21.6 (OCH_3). LR-MS *m/z*: 269 (M^+). HR-MS: Calcd for $C_{12}H_{15}NO_6$: 269.0900. Found: 269.0921.

$Co(OAc)_3$–$Cu(OAc)_2$ Oxidation of Arylacetic Acids (General Procedure) A mixture of arylacetic acid (1 mmol) and $Cu(OAc)_2$ (0.182 g, 1 eq) was added to a solution of $Co(OAc)_3$ in AcOH (0.33 mol/l, 7 ml, 2.3 eq), and the mixture was heated under reflux for 5—15 min. Water was added to the reaction mixture and the whole was extracted with ether. The organic layer was concentrated and the residue was purified by SiO_2 chromatography (AcOEt–hexane) and, if necessary, by HPLC (MeOH : H_2O = 3 : 1) to give the products (see Tables 1—3).

15: Oil. IR(neat): 1742, 1695, 1603, 1518, 1250, 1225. ^{1}H-NMR: 7.38 (2H, d, J=9.0 Hz, Ar-H), 6.88 (2H, d, J=9.0 Hz, Ar-H), 5.46 (1H, br s, =CH_2), 5.27 (1H, br d, J=1.1 Hz, =CH_2), 4.96 (2H, s, –CH_2–), 3.82 (3H, s, –OCH_3), 2.08 (3H, s, –$OCOCH_3$). ^{13}C-NMR: 170.8 (CO), 159.5 (C), 141.8 (C), 130.5 (C), 127.1 (CH), 127.1 (CH), 113.9 (CH), 113.9 (CH), 113.7 (CH_2), 65.9 (CH_2), 55.3 (CH_3), 21.0 (CH_3). LR-MS *m/z*: 206 (M^+). HR-MS: Calcd for $C_{12}H_{14}O_3$: 206.0942. Found: 206.0917.

$Mn(OAc)_3$ Oxidation of 20 in AcOH A solution of **20**[11] (0.220 g, 1 mmol) in AcOH (2 ml) was added to a refluxing solution of $Mn(OAc)_3 \cdot 2H_2O$ (0.616 g, 2.3 eq) in AcOH (8 ml) and heating was continued for 10 min. The reaction mixture was concentrated under reduced pressure. The residue was extracted with CH_2Cl_2 and insoluble Mn(II) was removed by filtration. Removal of the solvent from the filtrate and chromatography of the residue on a SiO_2 column with AcOEt–hexane (1 : 10) gave 67 mg (39%) of **21**. Further elution with AcOH–AcOEt–hexane (1 : 2 : 10) gave the starting material **20**, which was treated with diazomethane to give 60 mg (26%) of the corresponding methyl ester.

21: Colorless prisms from AcOEt–hexane. mp 83—85 °C. IR (KBr): 2950, 2900, 2845, 1605. ^{1}H-NMR: 7.36 (2H, d, J=8.8 Hz, Ar-H), 6.84 (2H, d, J=8.8 Hz, Ar-H), 6.03 (1H, t, J=2.1 Hz, =CH–), 3.79 (3H, s, –OCH_3), 2.78—2.38 (4H, m, =CH–CH_2), 2.15—1.82 (2H, m, –CH_2–). ^{13}C-NMR: 158.8 (C), 141.8 (C), 129.7 (C), 126.6 (CH), 126.6 (CH), 123.9 (CH), 113.6 (CH), 113.6 (CH), 55.2 (CH_3), 33.3 (CH_2), 33.3 (CH_2), 23.3 (CH_2). LR-MS *m/z*: 174 (M^+). HR-MS: Calcd for $C_{12}H_{14}O$: 174.1043. Found: 174.1023.

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