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# Oxidative cleavage of *β*-aryl alcohols using manganese(IV) oxide

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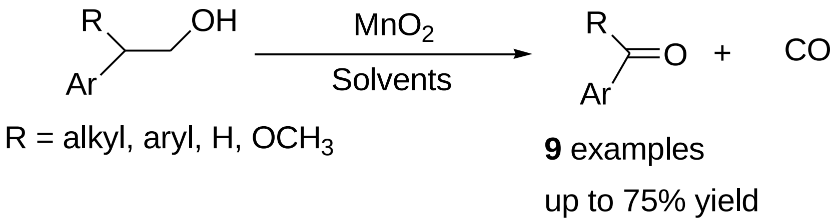
## Abstract

It was found that *β*-aryl alcohols can be cleaved to chain-shortened carbonyl compounds with direct formation of carbon monoxide by treatment with manganese(IV) oxide. A mechanistic scheme is proposed that accounts for the loss of one carbon atom. Carbon monoxide was detected by $PdCl_2$/HCl reagent.



**Keywords:** Oxidation, oxidative cleavage, manganese dioxide, alcohols

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## Introduction

Manganese(IV) oxide is a brown or black inorganic compound with empirical formula $MnO_2$. The main natural source of Mn(IV) oxide is the mineral pyrolusite. Mn(IV) oxide is an heterogeneous oxidizing agent which is cheap and non-toxic.[1–18] Commercial active Mn(IV) oxide is widely used as an oxidizing agent in preparative organic synthesis and in industry.

The precise structure of manganese(IV) oxide depends on the method of preparation. Pyrolusite (natural Mn(IV) oxide) and purely synthetic crystalline Mn(IV) oxide are weak oxidizing agents.[1] The oxidation of organic compounds requires activated Mn(IV) oxide, for the preparation of which several methods have been reported.[1–18] Depending on the preparative method, the structure, composition and the reactivity of the active Mn(IV) oxide changes. The efficiency of active Mn(IV) oxide strongly depends on the percentage of the *γ*-form. Active *γ*-Mn(IV) oxide is sometimes significantly more effective than classical Mn(IV) oxide.[17] It is also known that the water content of active Mn(IV) oxide has a strong influence on the oxidation power and the selectivity of its reactions. Manganese oxide, which contains water in 40-60% (weight%) is activated by heating at various temperatures (12-24 h at 100-130 °C).[19] If there is excess water, the oxidizing power of Mn(IV) oxide decreases.[18,20] According to a theory by Fatiadi *et al.*[1] the excess of water prevents the substrate from being selectively oxidized on the surface of the Mn(IV) oxide. On the other hand, the presence of hydrated Mn(IV) oxide is important to obtain an active reagent. For these reasons, the drying process must be carefully controlled.[2,13,18,21]

The choice of solvent is also very important for the use of Mn(IV) oxide in oxidations. Primary and secondary alcohols or water are normally not suitable as solvents because they are adsorbed on the active surface of Mn(IV) oxide and thus deactivate the reagent.[18] A similar influence is observed with polar solvents (acetone, EtOAc, DMF and DMSO). However, these solvents including water, acetic acid or pyridine can be used at high temperatures without any problems. In the literature, most reactions have been carried out in chlorinated hydrocarbons, diethyl ether, THF, EtOAc, acetone, acetonitrile or in ionic liquids. The best results for the oxidation of benzyl[15] and allyl alcohols[14,15] are achieved in diethyl ether.

Mn(IV) oxide is often used as an oxidizing agent in the following reactions:

- in the oxidation of allyl alcohols to *α,β*-unsaturated aldehydes or ketones.[22–30] In general, allyl alcohols can be oxidized with Mn(IV) oxide to the corresponding aldehydes with good-to-very good yields.[7–10,19,20,31] An important example for the oxidation of allyl alcohols is the preparation of retinal from vitamin $A_1$.[12]
- when converting allyl alcohols into *α,β*-unsaturated esters or amides.[20] The first method for conversion allyl alcohols into *α,β*-unsaturated esters and amides was developed by Corey *et al.*[20,25] The key step is the formation and subsequent oxidation of the cyanohydrin. The acyl cyanide initially formed by oxidation is converted into the corresponding *α,β*-unsaturated ester[25] or amide[20] by alcoholysis or aminolysis.
- in the oxidation of propargylic,[32] heterocyclic benzyl alcohols,[33] and *γ,δ*-unsaturated alcohols.[34] Propargylic alcohols can also be oxidized with Mn(IV) oxide to give alkynyl aldehydes or ketones.[32,35,36] The oxidation of heterocyclic benzyl alcohols[25,33] and *γ,δ*-unsaturated alcohols[34,37] with Mn(IV) oxide is very effficient. Oxidative cleavage of the C-C bond of 1,2-diols,[37] for example to produce the corresponding diketones[37] can also be achieved with manganese dioxide.
- when hydrating nitriles to amides,[38]
- in dehydration and aromatization reactions,[39]
- in the oxidation of amines to aldehydes, imines, amides and to diazo compounds.[40]

The oxidation of nitriles to amides with Mn(IV) oxide proceeds in good-to-very-good yields.[38] Manganese (IV) oxide reacts also with the following functional groups:

- with olefins as substrates for the cleavage of olefins or for the aromatization of cyclic olefins,[30,39,41,42]
- with amines as substrates, oxidation to amides, imines[40] or with *N-N* coupling to diazo compounds,[5]
- with diphenyl methanes as substrates, leaeding to oxidation to benzophenone[43] or with oxidative dimerization to 1,1,2,2-tetraphenylethane,[44]
- with aromatic aldehydes as substrates leading to oxidation to carboxylic acids[5],
- with phosphines as substrates leading to oxidation to phosphine oxides.[5]

Barakat *et al.* has shown that carboxylic acids (Table 1, entries 1-6), $\alpha$-hydroxycarboxylic acids (Table 1, entries 7-9) or $\alpha$-aminocarboxylic acids (Table 1, entries 10-13) react with Mn(IV) oxide with decarboxylation or with ammonia elimination producing the corresponding carbonyl compounds (Table 1). Barakat *et al.* assumed that the formation of ethylene from two citric acid molecules occurs through the reaction of two carbene intermediates. However, no additional experiments were carried out to detect the carbene intermediates (Table 1, entries 3-6).[5]

**Table 1.** Oxidation of carboxylic acids, $\alpha$-hydroxycarboxylic acids and $\alpha$-aminocarboxylic acids by Barakat *et. al.*[5]

| Entry | Substrate | Products | Yield (%) |
|---|---|---|---|
| 1 | HCOOH | $CO_2$ | -[a] |
| 2 | $PhCH_2CO_2H$ | PhCHO, $CO_2$ | 50, -[a] |
| 3 | $CH_2(CO_2H)_2$ | $C_2H_4$, $CO_2$ | - |
| 4 | $HO_2C(CH_2)_2CO_2H$ | $C_2H_4$, $CO_2$ | -[a] |
| 5 | maleic acid | $C_2H_2$, $CO_2$ | -[a] |
| 6 | fumaric acid | $C_2H_2$, $CO_2$ | -[a] |
| 7 | $HOCH_2CO_2H$ | $CO_2$ | -[a] |
| 8 | $CH_3CH(OH)CO_2H$ | MeCHO, $CO_2$ | 50,-[a] |
| 9 | $PhCH(OH)CO_2H$ | PhCHO, $CO_2$ | 50,-[a] |
| 10 | $H_2NCH_2CO_2H$ | $CO_2$, $NH_3$ | -[a] |
| 11 | $MeCH(NH_2)CO_2H$ | MeCHO, $CO_2$, $NH_3$ | -[a] |
| 12 | $Pr^iCH(NH_2)CO_2H$ | $Pr^iCHO$, $CO_2$, $NH_3$ | -[a] |
| 13 | $Bu^iCH(NH_2)CO_2H$ | $Bu^iCHO$, $CO_2$, $NH_3$ | -[a] |

[a] The yields are not given in the literature.[5]

The corresponding carbonyl compounds or carbon dioxide are formed during the oxidation of alcohols or 1,2-diols with manganese dioxide (Table 2).[5]

**Table 2.** Oxidation of alcohols with manganese dioxide by Barakat *et. al.* [5]

| Entry | Substrate | Products | Yield (%) |
|---|---|---|---|
| 1 | EtOH | MeCHO | 50 |
| 2 | $Pr^iOH$ | acetone | 50 |
| 3 | $Bu^iOH$ | $Pr^iCHO$ | 50 |

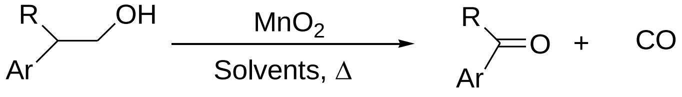
| | | | |
|---|---|---|---|
| 4[b] | $Ph_2CHOH$ | $(Ph_2CH)_2O$ | 88 |
| 5[c] | $Ph_2CHOH$ | benzophenone | 87 |
| 6 | 9-hydroxyfluorene | fluorenone | 86 |
| 7 | $(CH_2OH)_2$ | $CO_2$ | -[a] |
| 8 | $HOCH(CH_2OH)_2$ | $CO_2$ | -[a] |
| 9 | mannitol | $CO_2$ | -[a] |
| 10 | inositol | $CO_2$ | -[a] |

[a] The yields are not given in the literature. [b] The reaction was carried out in diethyl ether. [c] The reaction was carried out in benzene.[5]

## Results and Discussion

There are many examples of the oxidation of a broad range of organic functional groups in the literature. However, there exists only one example of the oxidative cleavage of alcohols.[50] In this work, a new oxidative cleavage method is presented to produce aldehydes/ketones starting from the corresponding *β*-aryl alcohols using manganese dioxide in nonpolar solvents (Table 3).

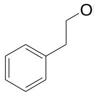
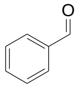
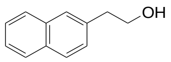
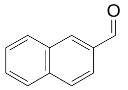
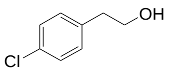
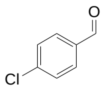
**Table 3.** The oxidative cleavage of alcohols to aldehydes or ketones

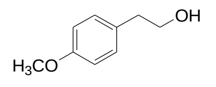
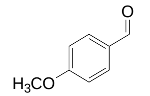
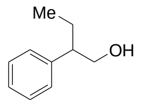
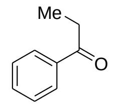
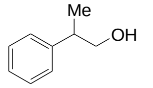
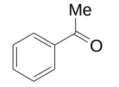
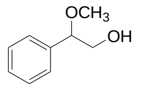
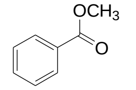
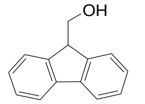
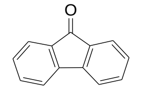
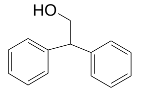
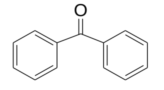


R = alkyl, aryl, H, $OCH_3$

**9 examples**

up to 75% yield

| | entry | substrate | product | reagent(s)[a] | Solvent | time | temp. (°C) | conver. (%) | yield (%)[d] |
|---|---|---|---|---|---|---|---|---|---|
| **A** | 1 |  |  | $MnO_2·Al_2O_3·SiO_2$ | cyclohexane | 1 day | rt | -[b] | **25** |
| **B** | 2 |  |  | $KMnO_4/MnO_2$ | acetone | 5 days | rt | 44 | **9** |
| | 3 | | | $MnO_2$ | $CHCl_3$ | 5 h | 56 | 59 | **18** |
| | 4 | | | $MnO_2$ | PE 60/70 | 1 h | 65 | 65 | **35** |
| **C** | 5 |  |  | $MnO_2$ | water | 1 day | 100 | **no reaction** | |
| | 6 | | | $MnO_2/H_2O_2$ | PE 60/70 | 1 day | rt | 5 | **3** |
| | 7 | | | $KMnO_4$[b] | acetone | 1 day | 56 | -[c] | **4** |
| | 8 | | | $KMnO_4/MnO_2$ | acetone | 5 days | rt | 66 | **4** |
| | 9 | | | $KMnO_4/MnO_2$ | acetone | 1 day | rt | 64 | **6** |
| | 10 | | | $MnO_2$/TBHP | PE 60/70 | 1 day | rt | 21 | **6** |
| | 11 | | | $KMnO_4$ | acetone | 5 days | rt | 53 | **8** |
| | 12 | | | $MnO_2$ | PE 30/50 | 6 days | rt | 47 | **11** |
| | 13 | | | $MnO_2$ | acetone | 16 h | 56 | 36 | **12** |
| | 14 | | | $MnO_2$ | PE 60/70 | 2 days | 65 | 52 | **12** |
| | 15 | | | $MnO_2$ | PE 60/70 | 1 day | 65 | 25 | **12** |
| | 16 | | | $KMnO_4$ | acetone | 6 h | rt | 43 | **12** |
| | 17 | | | $MnO_2/O_2$ | PE 60/70 | 1 day | 40 | 27 | **14** |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 18 | | | $MnO_2$ | 1,3-xylene | 5 days | 139 | 58 | **15** |
| | 19 | | | $MnO_2$ | PE 30/50 | 3 days | 40 | 56 | **20** |
| | 20 | | | $KMnO_4/MnO_2$ | PE 60/70 | 5 days | rt | 56 | **23** |
| | 21 | | | $MnO_2$ | $CHCl_3$ | 16 h | 61 | 30 | **23** |
| | 22 | | | $MnO_2 \cdot Al_2O_3 \cdot SiO_2$ | cyclohexane | 16 h | 80 | -[c] | **39** |
| **D** | 23 |  |  | $KMnO_4/MnO_2$ | acetone | 2 h | rt | -[c] | **5** |
| **E** | 24 |  |  | $MnO_2$ | PE 30/50 | 5 days | 40 | 20 | **20** |
| | 25 | | | $MnO_2$ | PE 60/70 | 16 h | 65 | 24 | **22** |
| | 26 | | | $KMnO_4/MnO_2$ | acetone | 1 day | rt | 64 | **24** |
| | 27 | | | $MnO_2$/KOH | PE 60/70 | 1 day | 65 | 70 | **30** |
| | 28 | | | $MnO_2$/KOH/AIBN | PE 60/70 | 1 day | 65 | 83 | **45** |
| | 29 | | | $MnO_2$/KOH/AIBN | cyclohexane | 1 day | 80 | -[c] | **54** |
| **F** | 30 |  |  | $MnO_2 \cdot Al_2O_3 \cdot SiO_2$ | cyclohexane | 17 h | 80 | -[c] | **34** |
| **G** | 31 |  |  | $KMnO_4/MnO_2$ | acetone | 1 day | rt | 94 | **34** |
| **H** | 32 |  |  | $MnO_2$/KOH/AIBN | cyclohexane | 1 day | rt | -[c] | **75** |
| **I** | 33 |  |  | $MnO_2 \cdot Al_2O_3 \cdot SiO_2$ | cyclohexane | 18 h | 80 | -[c] | **32** |

[a] *β*-Mn (IV) oxide (pyrolusite) was used in all reactions. The reagent is commercially available and was purchased from *Sigma-Aldrich* with MDL No.: MFCD00003463.[b]No selective reaction. [c]Not determined. [d] All yields were determined by the isolation of products.

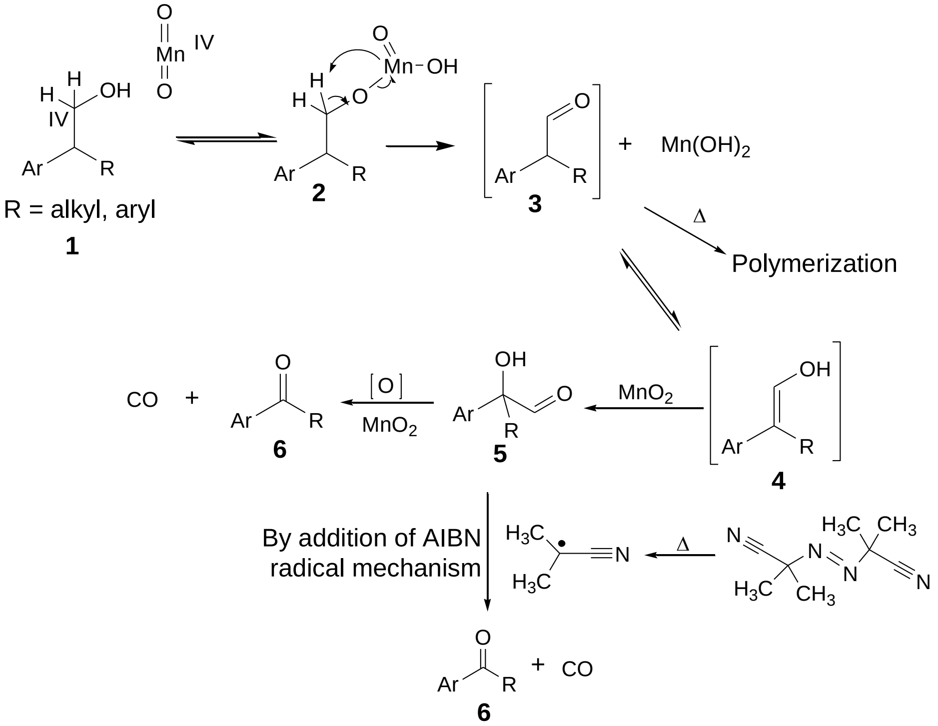
A total of nine substrates was tested (substrate A to substrate I) in different reaction conditions. However, yields of the oxidative cleavage vary and are low-to-good. For comparisons, the Table is separated into *β*-aryl alcohols (substrates A to D), *β*-aryl-*β*-alkyl alcohols (substrates E and F), *β*-aryl-*β*-methoxy alcohols (substrates G) and *β*,*β*-diaryl alcohols (substrate H and I) (Table 3). Substrate A cleaves oxidatively to benzaldehyde in 25% yield with manganese dioxide as the oxidizing agent, supported on aluminum silicate (entry 1, Table 3).[43] Substrate B reacts under oxidative cleavage to give 2-naphthaldehyde in very low yield using potassium permanganate and manganese dioxide as the oxidizing agent and using a polar solvent such as acetone (entry 2, Table 3). The best yield was achieved by using non-polar solvent petroleum ether 60/70 (entry 4, Table 3). Substrate C was also tested by using different polar solvents and by addition of different oxidizing agents to manganese dioxide such as $O_2$, $KMnO_4$, *tert*-butyl hydroperoxide, $H_2O_2$, $Al_2O_3/SiO_2$ in order to increase the activity of the manganese dioxide and thus the yield of the product (entries 5-22, Table 3). The oxidative cleavage was supposed to be accelerated because the conversion is still high and there was still a lot of starting material that did not undergo oxidative cleavage. The best yield was achieved by using cyclohexane as the non-polar solvent and manganese dioxide as the oxidizing agent, supported on aluminum silicate (entry 22, Table 3). Manganese dioxide is known to exhibit poor activity in polar solvents, as described in the introduction. For this reason, it was suspected that the yield of product using substrate D is low because polar solvents such as acetone were used (entry 23, Table 3).

The assumption was, that the oxidative cleavage would proceed by a radical mechanism pathway, because very little polymer was always obtained. Therefore, when optimizing the reactions with *β*-aryl- *β*-alkyl alcohols, azobis(isobutyronitrile) AIBN was added as a radical starter. The best yield was obtained with cyclohexane as solvent (substrates E, entry29, Table 3). Substrate F reacts with the use of manganese dioxide on aluminum silicate to acetophenone with moderate yield (entry30, Table 3).

2-Methoxy alcohol (substrates G) reacts under the same reaction conditions to give ester with moderate yield. That is one of the most important results of our research. If the reaction conditions could be optimized for a broad range of substrates, the corresponding esters could be prepared directly from 2-methoxy-1-alcohols, which is not yet known in the literature and would be very a useful method (entry31, Table 3).

In general, it can be said that *β*,*β*-diaryl alcohols (substrates H and I) are more reactive compared to *β*-aryl alcohols (substrates A to D) or *β*-aryl-*β*-alkyl alcohols (substrates E and F). Better yields were therefore obtained (entry 32, 33, Table 3). The assumption is that the *β*,*β*-diaryl alcohols are better able to form enol intermediates (see intermediate **4**, mechanism) during the reaction and that intermediate **5** can be formed more easily.[45]

*Mechanism*



**Scheme 1.** Proposed reaction mechanism of oxidative cleavage of *β*-aryl alcohols

Here, the effect of permanganate on the reaction mechanism was not considered. The subject of the paper is oxidation with Mn(IV), use of Mn(VII) is not included. It is assumed that *β*-aryl alcohol first oxidizes to the corresponding aldehyde **2** (Scheme 1). In this step, *α*-aryl aldehyde **3** can polymerize. *α*-Aryl aldehyde **3** is known to polymerize when heated.[5] Compound **3** or **4** react again through oxidation to give *α*-hydroxy, *α*-aryl aldehyde **5**. This can be cleaved to the corresponding product **6** either in the presence of AIBN and by a radical pathway or again by further oxidation by manganese(IV) oxide. This would produce carbon monoxide which was detected with $PdCl_2$/HCl reagent.[46] For this, a bubble counter was filkled with the yellowish liquid, which was connected directly to the round-bottom flask or reflux condenser. Attempted detection of carbon dioxide, with $Ba(OH)_2$,[47] in all reactions gave a negative result.

## Conclusions

The development of new methods with heterogeneous reagents that are easy to prepare and easy to separate from the reaction environment is particularly important for organic synthesis. Manganese(IV) oxide can be counted among such reagents. It was shown for the first time that *β*-aryl alcohols are oxidatively cleaved with Mn(IV) oxide to the corresponding aldehydes. However, the conversion and yield of the reaction are only low-to-good. It is possible that conversions and yields could be increased by switching to non-polar solvents (e.g. petroleum ether).

## Experimental Section

### Methods and analysis methods

### 1. Solvents

Solvents were dried using standard methods. Cyclohexane, ethanol, benzene and toluene were dried over sodium, distilled off and stored over molecular sieves 3Å or 4Å under argon. Methanol was dried over magnesium, distilled and stored over 3 Å molecular sieves under argon. 1,4-Dioxane, THF and diethyl ether were first dried over potassium hydroxide, then over sodium, distilled and stored over molecular sieve 4 Å under argon. EtOAc and acetone were dried over phosphorus pentoxide, distilled and stored over molecular sieves 4Å or 3Å under argon. Dichloromethane was dried over potassium carbonate and distilled. Chloroform and the remaining chlorinated and/or fluorinated solvents were freshly distilled before use. Working with exclusion of air and moisture was carried out under an inert gas atmosphere (argon 5.0 from the company "*Sauerstoffwerk Friedrichshafen GmbH*"). *β*-Mn (IV) oxide (pyrolusite) was used in all reactions. The reagent is commercially available and was purchased from *Sigma-Aldrich* with MDL No.: MFCD00003463.

### 2. Chromatography

Analytical thin-layer chromatography on silica gel foils (silica gel 60 $F_{254}$) from E. Merck, Darmstadt or aluminum oxide foils ($Al_2O_3$ 150 $F_{254}$) from Mancherey-Nagel GmbH & Co. KG. The substances were detected by UV light ($\lambda$ = 254 nm), staining with iodine or the spray reagent 2,4-dinitrohydrazine solution.

The preparative column chromatography was carried out in gravity columns with silica gel 60 (0.06-0.2 mm) from Roth. The cyclohexane and EtOAc solvents used were distilled before use.

### 3. Gas chromatography and HPLC

The analytical gas chromatography was carried out on the devices:

Achiral GC: 6890N from agilent technologies (column used: 122-7032 DB-WAX 30m x 0.25 mm x 0.25 µm).

Chiral GC: 6890N from Agilent Technologies (column used: hydrodex-β-TBDAc 25 mx 0.25 mm ID, cyclodextrin is not chemically linked to polysiloxane here).

The analytical HPLC separations were carried out on the following device:

Merck-Hitachi, L-7100 (pump), D-7000 (detector) (column and solvent used: chiralpak AD-H, *n*-heptane/IPA in different ratios).

### 4. Mass spectrometry and GC / MS

When evaluating a GC / MS-EI, GC / MS-CI or MS-EI spectrum, the peaks, whose intensity is below 0.5, 1, 3 or 10%, were neglected.

*Electron impact ionization (EI)*: TSQ 700 and MAT 95XL (Fa. thermo), ionization energy 70 eV, source temperature 200 °C
*Chemical ionization (CI)*: TSQ 700 and MAT 95XL (Fa. thermo), ionization energy 110 eV, source temperature 200 °C, ammonia was used as the collision gas.
GC / MS-EI: TSQ 700 with varian 3400.
GC / MS-CI: TSQ 700 with varian 3400, ammonia was used as the collision gas.
*Electrospray ionization (ESI): TSQ 7000 (thermo)*
2.5 µl sample solution / min. are in a flow of 100 µl / min. acetonitrile introduced: spray voltage: 5 kV (spray current: 5 µA); average10; cap.: 300 °C

## 5. Nuclear magnetic resonance spectroscopy

The nuclear magnetic resonance spectra were measured on the devices of the types DRX 250, Avance II 400, DRX 500 from Bruker and Mercury 300 from Varian. In the case of $^1$H nuclear magnetic resonance, the chemical shifts were supported on the residual proton content of the deutero-chloroform used as the solvent ($CDCl_3$, $\delta$ = 7.26 ppm), deutero-dichloromethane ($CD_2Cl_2$, $\delta$ = 5.32 ppm), deutero-dimethyl sulfoxide (DMSO-$d_6$, $\delta$ = 2.54 ppm), deutero-water ($D_2O$, δ = 4.79 ppm), deutero-acetone (acetone-$d_6$ = 2.09 ppm) or deutero trifluoroacetic acid (TFA-$d$ = 11.5 ppm). In the $^{13}$C nuclear magnetic resonance, the deuterium-coupled signal at $\delta$ = 77.1 ppm ($CDCl_3$), $\delta$ = 206 ppm (acetone-$d_6$), $\delta$ = 39.5 ppm (DMSO-$d_6$) or $\delta$ = 164.2 ppm (TFA-$d$) served as references, In $^{19}$F-NMR measurements in deutero-chloroform, the magnetic field was accordingly lured with $^1$H-NMR. In TFA-d the signal at $\delta$ = -78.14 ppm served as a reference.

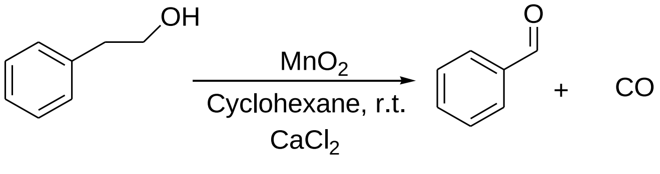
The following abbreviations were used to describe the signal multiplicities:
s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, bs = broad singlet, dd = double doublet, dt = double triplet, td = triplet doublet, tt = triplet triplet, dq = double quartet.

## Synthesis of manganese(IV) oxide supported on aluminum silicate ($Al_2O_3{\cdot}SiO_2$)[43]

$$KMnO_4 + MnSO_4{\cdot}H_2O \rightarrow MnO_2{\cdot}Al_2O_3{\cdot}SiO_2$$

Aluminum silicate (30 g) was added to a solution of $KMnO_4$ (1.9 g) in destilled water (50 mL). The water was then removed. The powder was ground and added to a solution of $MnSO_4$ (4.9 g) in water (50 mL). Then it was filtered through Celite and washed with plenty of water. Then it was dried in a drying oven for three days.

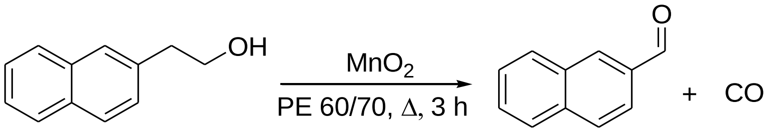
## Substrate A (entry 1, Table 3)



Into a dry round-bottomed flask flushed under counter flow of argon was added Mn(IV) oxide (3.8 g, 3.5 mmol) in cyclohexane (20 mL) and $CaCl_2$ (1 g). Substrate A was dissolved in cyclohexane (15 mL) and slowly injected into the suspension. The suspension is stirred for one day in rt. Next, EtOAc (approx. 50 mL) was added and the mixture filtered through Celite, dried with a little $MgSO_4$ and filtered again. The solvent was removed. The product was isolated by column chromatography (eluent: PE : $CH_2Cl_2$ = 1: 2)

$^1$H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 - 7.51 (m, 2 H) 7.52 - 7.62 (m, 1 H) 7.75 - 7.89 (m, 2 H) 9.96 (s, 1 H).$^{13}$C NMR (25 MHz, $CDCl_3$) δ ppm 191.6, 161.6, 132.5, 129.9, 116.0. FTIR (thin film) cm$^{-1}$ 3577, 3403, 3054, 3031, 2958, 2870, 2339, 1953, 1886, 1809, 1701, 1601, 1495, 1453, 1386, 1266, 1206, 1073, 1023, 917, 812, 559, 464.

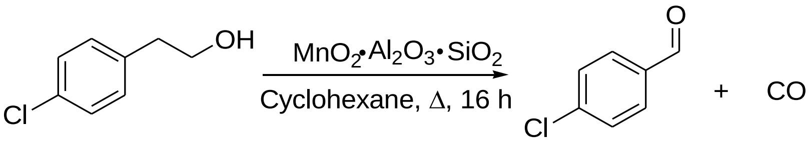
**Substrate B (entry 4, Table 3)**



344 mg (2 mmol, 1 eq.) 2-(2-naphthyl) ethanol was dissolved in 30 mL PE 60/70 (abs.). 512 mg (4 mmol, 2 eq.) manganese dioxide are added. The black suspension is heated under reflux for 3 h. It was cooled to rt and filtered through Celite. The solvent was then removed. (eluent: cyclohexane:EtOAc = 50: 1 → 20: 1 → 10: 1).

$^1$H NMR (300 MHz, $CDCl_3$) δ ppm 7.54 - 7.70 (m, 2 H) 7.88 - 8.07 (m, 4 H) 8.33 - 8.37 (m, 1 H) 10.17 (s, 1 H). $^{13}$C NMR (75 MHz, $CDCl_3$) *δ* ppm 192, 136, 134, 134, 132, 129, 129, 128, 127, 122. FTIR (KBr disc) cm$^{-1}$ 3368, 3065, 2847, 2631, 1695, 1656, 1627, 1597, 1578, 1451, 1441, 1403, 1364, 1346, 1267, 1257, 1215, 1167, 1149, 1143, 1119, 1008, 986, 955, 909, 879, 872, 837, 822,773, 752, 628, 606, 484, 478. GC/MS-EI *m*/*z*(%): 157.1(11), 156.1(>100), 155.1(94), 128.1(12), 127.1(60), 126.1(11), 101.1(3), 77.2(4), 75.1(3).

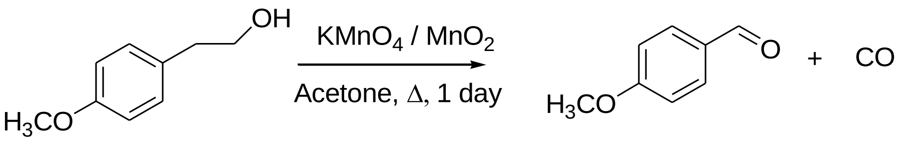
**Substrate C (entry 22, Table 3)**



105.2 mg (0.67 mmol, 1 eq.) 2-(4-chlorophenyl) ethanol was dissolved in 25 mL cyclohexane (abs.) and 5 g manganese dioxide on aluminum silicate was added. The black suspension was heated under reflux for 16 h. The suspension was cooled to rt and filtered through Celite and washed with copiious EtOAc. The solvent was removed under reduced pressure. The product was purified by column chromatography (eluent: cyclohexane: EtOAc 3: 1)

$^1$H NMR (300 MHz, $CDCl_3$) δ ppm 7.52 (d, *J* = 8.35 Hz, 2 H) 7.83 (d, *J* = 8.64 Hz, 2 H) 9.99 (s, 1 H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ ppm 191, 142, 135, 131, 128. FTIR (KBr disc.) cm$^{-1}$ 3089, 2860, 2855, 2769, 2759, 2745, 1919, 1699, 1693, 1678, 1597, 1588, 1577, 1486, 1419, 1388, 1362, 1321, 1293, 1265, 1209, 1163, 1155, 1131, 1094, 1081, 1012, 841, 817, 794, 705, 700, 629, 544, 481.

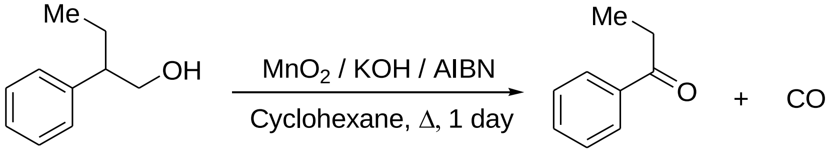
**Substrate D (entry 23, Table 3)**



500 mg (3.3 mmol, 1 eq.) 2-(4-methoxyphenyl)-ethanol was dissolved in 50 mL acetone (abs.). 571 mg (6.6 mmol, 2 eq.) manganese(IV) oxide and 1.04 g (6.6 mmol, 2 eq.) potassium permanganate were added. The black / dark red suspension was heateed at reflux for 1 day. It was cooled to rt and filtered through Celite. The product was isolated using column chromatography (eluent: cyclohexane / EtOAc = 20: 1).

$^1$H NMR (300 MHz, $CDCl_3$) δ ppm 3.73 (s, 3H) 6.96 (d, J=8.35 Hz, 2 H) 7.70 (d, J=8.64 Hz, 2 H) 9.87 (s, 1 H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ ppm 191, 164, 134, 131, 115, 55. FTIR (thin film) cm$^{-1}$ 3077, 3010, 2969, 2938, 2911, 2841, 2806, 2740, 1698, 1601, 1578, 1511, 1461, 1443, 1427, 1394, 1316, 1302, 1261, 1216, 1182, 1151, 1109, 1025, 855, 834, 767, 759, 645, 632, 608, 596, 517.

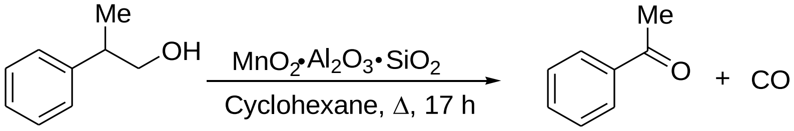
**Substrate E (entry 29, Table 3)** [49]



100 mg (0.666 mmol, 1 eq.) 2-phenyl-1-butanol was dissolved in 300 mL cyclohexane. Then 116 mg (1.33 mmol, 2 eq.) Mn(IV) oxide, 112 mg (2 mmol, 3 eq.) KOH, 11 mg (0.067 mmol, 0.1 eq.) AIBN and 5 drops of acetone were added and the mixture heated under reflux for 1 day. After cooling, the suspension was filtered through Celite and the solvent removed. The product was isolated by column chromatography (eluent: cyclohexane: EtOAc: 20: 1)

$^1$H NMR (300 MHz, $CDCl_3$) δ ppm 1.16 (t, 3 H) 2.95 (d, J=7.33 Hz, 2 H) 7.28 - 7.61 (m, 3 H) 7.70 - 8.13 (m, 2 H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ ppm 201, 136, 132, 128, 127, 31, 9.

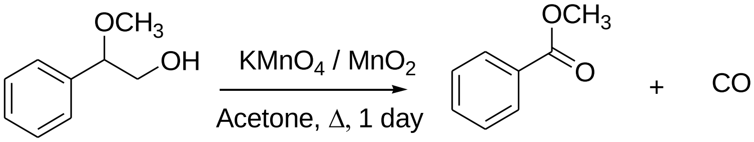
**Substrate F (entry 30, Table 3)** [48]



91 mg (0.67 mmol) of 2-phenyl-1-propanol was dissolved in 25 mL of cyclohexane and 5 g of manganese dioxide on aluminum silicate added. The suspension was heated under reflux for 17 h. The suspension was then filtered through Celite and washed with copious EtOAc. The solvent was removed under reduced pressure and the product purified by column chromatography (eluent: cyclohexane: EtOAc = 20: 1 → 3: 1).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 2.61 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.2, 137.1, 133.1, 128.6, 128.3, 26.6. FTIR (thin film) cm$^{-1}$ 3604, 3352, 3087, 3069, 3040, 3029, 3006, 2967, 2925, 2887, 1686, 1646, 1599, 1583, 1546, 1492, 1450, 1430, 1360, 1313, 1303, 1257, 1181, 1150, 1109, 1079, 1025, 1001, 966, 928, 761, 731, 691, 616, 588.

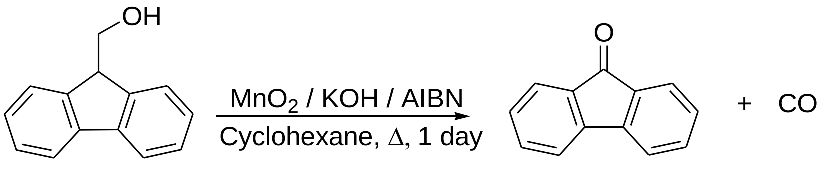
**Substrate G (entry 31, Table 3)**



500 mg (3.3 mmol, 1 eq.) 2-methoxy-2-phenylethanol was dissolved in 50 mL acetone (abs.). 571 mg (6.6 mmol, 2 eq.) manganese(IV) oxide and 1.04 g (6.6 mmol, 2 eq.) potassium permanganate were added. The black/dark red suspension was heated under reflux for 1 day then filtered, cooled to rt and filtered through Celite. The product was isolated using column chromatography (mobile phase: cyclohexane / EtOAc = 20: 1)

$^1$H NNMR (400 MHz, $CDCl_3$): δ 8.20-8.00 (d, J = 8 Hz, 2H), 7.60-7.50 (m, 1H), 7.50-7.41 (m, 2H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): 166.8, 132.9, 130.5, 129.7, 128.5, 51.8.

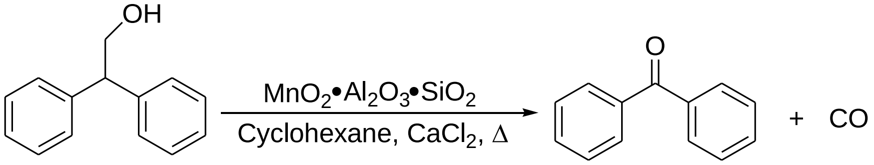
**Substrate H (entry 32, table 3)**[50]



131 mg (0.667 mmol, 1 eq.) 9-fluorenylmethanol were dissolved in 300 mL cyclohexane. 116 mg (1.33 mmol, 2 eq.) Mn(IV) oxide, 112 mg (2 mmol, 3 eq.) KOH, 11 mg (0.066 mmol, 0.1 eq.) AIBN and 5 drops of acetone were added. The suspension was heated at reflux for 1 day. After cooling, the suspension was filtered through kieselguhr and the solvent removed. The product was isolated by column chromatography (eluent: cyclohexanes: EtOAc = 50: 1 → 20: 1 → 10: 1 → 1: 1).

yellow solid powder; m.p. 80-82 °C (81-83 °C); $^1$H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.48-7.45 (m, 4H), 7.28-7.26 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ 193.8, 144.3, 134.6, 134.0, 129.0, 124.2, 120.2.

**Substrate I (entry 33, Table 3)** [49]



198.3 mg (1 mmol) $MnO_2{\cdot}Al_2O_3{\cdot}SiO_2$ and 1.5 g $CaCl_2$ were placed in 35 mL cyclohexane under argon. The substrate was dissolved in 10 mL cyclohexane and added using a syringe The residue rinsed with 5 mL cyclohexane and this added to the suspension. The suspension was heated under reflux and argon for 18 h. After cooling, the suspension was filtered through Celite and washed with TBME. The product was isolated by column chromatography (eluent: PE 60/70: methylene chloride = 1: 2)

Benzophenone: white crystal; m.p. 47-49 °C (47-49 °C, lit.); H-NMR (250 MHz, $CDCl_3$): δ 7.80 (d, 4H, *J* = 8.25 Hz), 7.61-7.44 (m, 6H). $^{13}$C NMR (62.98 MHz, $CDCl_3$): δ 196.7, 137.5, 132.4, 130.0, 128.2.

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## Supplementary Material

NMR, IR spectra of the compounds in Table 3 are available.

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