Transition-Metal-Catalyzed Oxidations, 2[1]

Titanium- or Zirconium-Catalyzed Selective Dehydrogenation of Benzyl Alcohols to Aldehydes and Ketones with *tert*-Butyl Hydroperoxide

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Primary and secondary benzyl alcohols are selectively converted in high yields into the corresponding aldehydes or ketones using *tert*-butyl hydroperoxide and catalytic amounts of titanium or (better) zirconium alcoholates. Aliphatic hydroxy groups, double bonds (except those in allylic position to hydroxy groups), and phenolic hydroxy groups (except those in *ortho* position to the benzylic alcohol) are not attacked.

Recently, we described the transition-metal-mediated specific oxidation of phenols to *ortho*-quinones[1]. The *ortho* selectivity of the oxygen transfer step was due to the simultaneous coordination of substrate and oxidant (*tert*-butyl hydroperoxide, TBHP) to the transition metal. In a subsequent experiment, benzyl alcohol was treated with $Ti(OiPr)_4$ and TBHP to see whether oxygen transfer to *non*-phenolic aromatic rings is also possible[2]. Instead of oxygenation, a clean dehydrogenation to benzaldehyde was observed. We now report the results of our systematic investigation of the transition-metal-catalyzed dehydrogenation of benzyl alcohols.

Selective oxidation of benzylic alcohols in the presence of other primary or secondary alcohols is a frequently encountered synthetic problem. The reagent of choice, activated manganese dioxide[3-6], suffers from several drawbacks. First, a high, often tenfold excess of reagent has to be used, which makes larger scale reactions a serious problem. Secondly, activated MnO_2 tends to adsorb certain substrates tightly, which then have to be washed out with large amounts of solvent. A certain degree of selectivity towards benzylic alcohols is also observed with chromium(VI) species under phase transfer conditions (e.g. orange benzene) using Adogen 464[7,8], 4-(dimethylamino)pyridinium chlorochromate[9], a catalytic procedure using chromium(VI) oxide and TBHP[10], or a bimetallic tin–chromium catalyst $(nBu_3Sn)_2CrO_2$[11a] in the presence of a large excess of TBHP. However, in all of these systems the oxygenation is not clearly decoupled from dehydrogenation and, moreover, TBHP is decomposed rather rapidly by chromium species. A selective oxidation of secondary hydroxy groups with respect to primary alcohols was observed with the $VO(acac)_2$/TBHP system[11b]. For related reactions mediated by molybdenum or selenium species compare ref.[11c].

If no selectivity in the oxidation of alcohols to aldehydes is required, the chromium-based reagents are most often employed[8,12-15]. Normally, the chromium(VI) reagents have to be used in large excess and chromatography is necessary to purify the products and remove chromium species. In addition, the use of this toxic heavy metal causes increasing environmental problems.

Procedure and Kinetics

The catalytic dehydrogenation procedure developed in our laboratory suffers from none of these disadvantages and is highly selective for the conversion of *benzylic* alcohols into the corresponding aldehydes or ketones. Primary or secondary *non*-benzylic aliphatic alcohols are virtually not attacked at all, nor are isolated or even homoallylic double bonds. The procedure is truly catalytic; only 10 mol-% of the nontoxic and relatively cheap, commercially available titanium or zirconium alcoholates $Ti(OiPr)_4$ and $Zr(OnPr)_4$ are required, in the presence of 1.5 mol of TBHP. TBHP is considered as "one of the best sources of oxygen atoms for a variety of organic oxygenations"[16]. The preparation and safe handling of dry dichloromethane solutions of TBHP is mainly based on the intensive investigations of Sharpless and co-workers[17]. The yields of the dehydrogenation of benzylic alcohols in the zirconium-catalyzed reactions were usually quantitative (TLC analysis).

In the first set of experiments the dehydrogenation of the mono-, di-, and trinuclear primary benzyl alcohols **1–11**, **23**, **25**, **27**, and **28** was investigated. Initially, one equivalent of $Ti(OiPr)_4$ and 1.5 mol of TBHP in dichloromethane was used (entry 32, Table 1). When the amount of the catalyst was systematically reduced to 10 mol-%, the reaction stopped at about 70% conversion of the benzyl alcohol after 24 h and the reaction solution smoothly solidified to a gel. Evidently, the catalyst was hydrolyzed by the water formed in the dehydrogenation process. Yields were considerably improved (to about 90%, see Table 1), when the water was trapped by addition of 3 Å molecular sieves (compare ref.[17,18]). With the titanium catalyst, most benzyl alcohols were smoothly converted into the corresponding aldehydes

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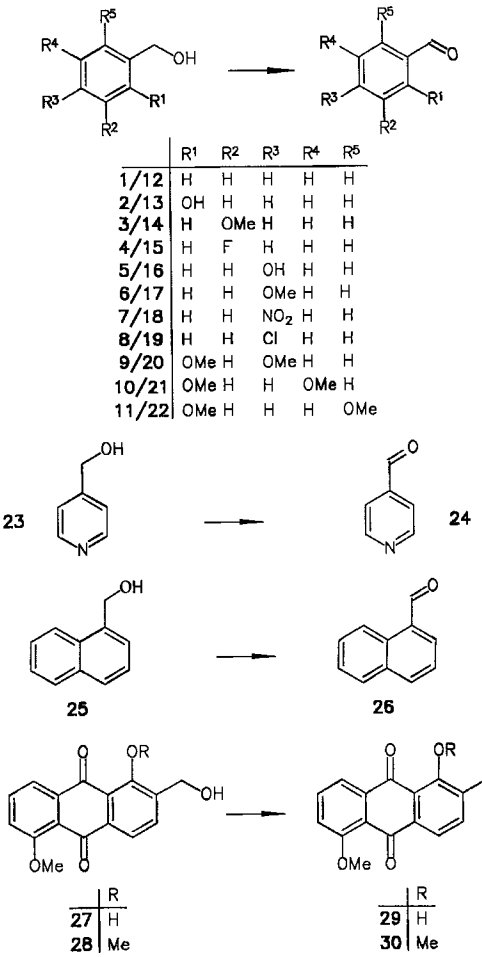
after 24 h of reaction time. However, the reaction rates were quite slow in the presence of electron acceptors (entry 15) and phenolic hydroxy groups in *para* position (entry 8, starting materials were recovered). In addition, acetone was formed at prolonged reaction times (16% after 24 h) by dehydrogenation of the 2-propanol present in the $Ti(OiPr)_4$ catalyst, using up some of the TBHP. This was shown in an NMR experiment (400 MHz) in the titanium-catalyzed dehydrogenation of **3**, monitoring simultaneously the formation of aldehyde **14** and acetone (see Experimental, Table 5). The process was *not* due to the activity of $Ti(OiPr)_4$ as a Meerwein-Ponndorf-Verley catalyst, as was shown in a control experiment. No acetone was formed after 24 h in a mixture of $Ti(OiPr)_4$, TBHP, and excess benzaldehyde. In a search for more active catalysts, the alcoholates $VO(acac)_2$ and $Zr(OnPr)_4$ were tried in the dehydrogenation reaction. In an NMR experiment, rapid conversion of 3-methoxybenzyl alcohol (**3**) was observed with $VO(acac)_2$ as catalyst, but 3-methoxybenzoic acid was formed in addition to the aldehyde **14**. Secondary benzyl alcohols such as **32** were, however, cleanly converted into the corresponding ketones (entry 28). The formation of benzoic acids was *never* observed in any zirconium-catalyzed reaction. Yields were essentially quantitative within much shorter reaction times than for the titanium-catalyzed reactions (compare entries 4/5, 8/9, 10/11, 15/16, 24/25, 26/27; Table 1). With the exception of electron-deficient substrates such as 4-nitrobenzyl alcohol (**7**) (entry 16), most zirconium-catalyzed reactions were completed within 3–7 h (entries 5, 6, 9, 11, 12, 14, 17, 27, 29–31, 36), though some reactions were continued overnight for reasons of convenience (entries 3, 21, 25, 33, 34). Even substrates with electron acceptors (such as **4** and **7**; entries 7 and 16) or *para*-hydroxy groups (**5, 40**; entries 9 and 34) gave very good yields of the aldehyde **16** and the ketone **42**. The formation of mixed acetals derived from **16** was observed in the reaction of **5** when molecular sieves purchased from Merck (instead of the normally employed Aldrich product) were used. However, this mixture of acetals could be hydrolyzed to **16** quantitatively. The reactions were mostly run in dichloromethane, but other solvents such as acetone, tetrahydrofuran and ethyl acetate could also be used (entries 5, 12, and 13, respectively). In apolar solvents (pentane; entry 14, and also in toluene) the reaction was much slower, yields were lower, and a black precipitate of unknown nature was formed. However, mixtures of these nonpolar solvents with 50% dichloromethane again produced the usually observed high yields. Steric hindrance by one *ortho* substituent had little effect on reaction rates and yields (substrates **9, 10, 28**, and **44**; entries 18, 19, 25, 36). However, severe steric hindrance caused by two neighboring methoxy groups such as in 2,6-dimethoxybenzyl alcohol (**11**) prevented dehydrogenation under the mild reaction conditions (entry 20). Another limitation of the method was seen in chelate-forming substrates as the *ortho*-phenols **2** and **27** and the 4-hydroxymethylpyridine **23**, in which reaction rates and yields decreased. Interestingly, 2-hydroxymethylpyridine was also not attacked by 4-(dimethylamino)pyridinium chlorochromate[9]. In the zirconium-catalyzed reactions this is interpreted as perturbation of a favorable six-membered transition state for hydrogen transfer (see below).



All experiments shown in Table 1 were monitored by TLC, but more accurate information was necessary to evaluate the catalytic activity of the catalysts and to optimize reaction conditions. The catalytic activities of $Ti(OiPr)_4$ and $Zr(OnPr)_4$ were compared in a set of kinetic experiments using ^{1}H-NMR spectroscopy to monitor the reactions (for details see Experimental). The yields of 3-methoxybenzal-

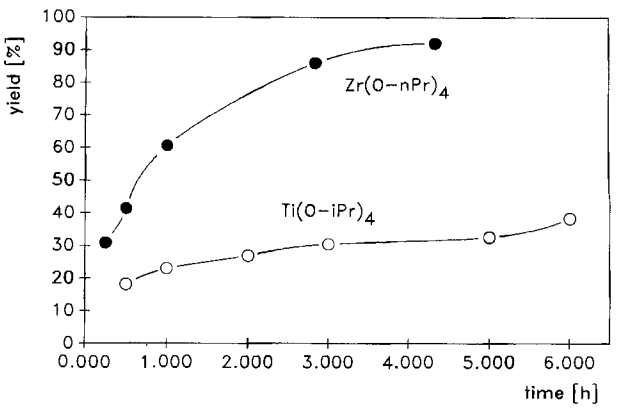


Figure 1. Yields of 3-methoxybenzaldehyde (**14**) in the $Ti(OiPr)_4$- and $Zr(OnPr)_4$-catalyzed dehydrogenations of **3** (1 equiv. of TBHP)

Table 1. Yields and conditions in the transition-metal-catalyzed dehydrogenation of primary and secondary benzylic alcohols with TBHP

Entry	Alcohol	Catalyst [mol-%]	t [h]	Product	Yield (%)
1	**1**	$Ti(OiPr)_4$, 10	24	**12**	91
2	**1**	$Ti(OiPr)_4$, 10	12	**12**	88[a]
3	**2**	$Zr(OnPr)_4$, 10	12	**13**	18
4	**3**	$Ti(OiPr)_4$, 10	24	**14**	86
5	**3**	$Zr(OnPr)_4$, 10	4	**14**	97[b]
6	**3**	$Zr(OnPr)_4$, 10	4	**14**	98
7	**4**	$Zr(OnPr)_4$, 20	5	**15**	98
8	**5**	$Ti(OiPr)_4$, 10	24	**16**	14
9	**5**	$Zr(OnPr)_4$, 10	3	**16**	74
10	**6**	$Ti(OiPr)_4$, 10	24	**17**	86
11	**6**	$Zr(OnPr)_4$, 10	5	**17**	98
12	**6**	$Zr(OnPr)_4$, 10	5	**17**	95[c]
13	**6**	$Zr(OnPr)_4$, 10	24	**17**	95[d]
14	**6**	$Zr(OnPr)_4$, 10	5	**17**	60[e]
15	**7**	$Ti(OiPr)_4$, 10	24	**18**	32
16	**7**	$Zr(OnPr)_4$, 20	6	**18**	98
17	**8**	$Zr(OnPr)_4$, 30	7	**19**	88
18	**9**	$Ti(OiPr)_4$, 10	24	**20**	89
19	**10**	$Ti(OiPr)_4$, 10	24	**21**	91
20	**11**	$Zr(OnPr)_4$, 10	12	**22**	4
21	**23**	$Zr(OnPr)_4$, 100	12	**24**	10
22	**25**	$Ti(OiPr)_4$, 10	24	**26**	77
23	**27**	$Ti(OiPr)_4$, 35	72	**29**	42
24	**28**	$Ti(OiPr)_4$, 10	24	**30**	41
25	**28**	$Zr(OnPr)_4$, 10	12	**30**	97
26	**31**	$Ti(OiPr)_4$, 10	24	**35**	92
27	**31**	$Zr(OnPr)_4$, 10	6	**35**	92
28	**32**	$VO(acac)_2$, 10	12	**36**	98
29	**32**	$Zr(OnPr)_4$, 10	4	**36**	98
30	**33**	$Zr(OnPr)_4$, 20	6	**37**	92
31	**34**	$Zr(OnPr)_4$, 10	6	**38**	96
32	**39**	$Ti(OiPr)_4$, 100	18	**41**	82
33	**39**	$Zr(OnPr)_4$, 10	18	**41**	97
34	**40**	$Zr(OnPr)_4$, 10	18	**42**	96
35	**43**	$Ti(OiPr)_4$, 10	24	–	–
36	**44**	$Zr(OnPr)_4$, 10	3	**45**	89

[a] 20 mmol of **1**, Kugelrohr distillation. – [b] In acetone. – [c] In THF. – [d] In ethyl acetate. – [e] In pentane.

dehyde (**14**) formed under identical conditions in the titanium- and zirconium-catalyzed reactions (see Experimental, Tables 2 and 4) are compared in Figure 1. The superiority of the zirconium complex is clearly demonstrated. (Note that only one equivalent of TBHP per alcohol was employed in the NMR experiments, and thus no quantitative conversion could be expected.) The half-life of 3-methoxybenzyl alcohol (**3**) was calculated from these data to be 37 min for $Zr(OnPr)_4$ and ca. 7 h for $Ti(OiPr)_4$. No dehydrogenation of the 1-propanol present as ligand in the zirconium catalyst was observed.

The influence of substituents on the aromatic nucleus was measured in competition experiments. The formation of 3-methoxybenzaldehyde (**14**) and 4-nitrobenzaldehyde (**18**) was compared (Table 2) and the data are plotted in Figure 2, showing the much more rapid conversion of the methoxy-substituted substrate **3**. Similar results were obtained by comparing the rates in the reaction of 3,4-methylenedioxybenzyl alcohol and 4-nitrobenzyl alcohol (see Experimental, Table 3). The rate acceleration in the donor-substituted substrate **3** compared to **7** has relevance for mechanistic considerations (see below). Preliminary kinetic experiments also indicated a nonlinear correlation between reaction rate and the concentration of the catalyst, similar to enzyme kinetics.

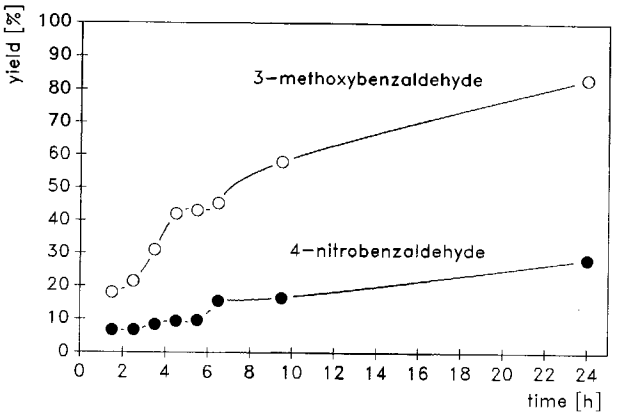


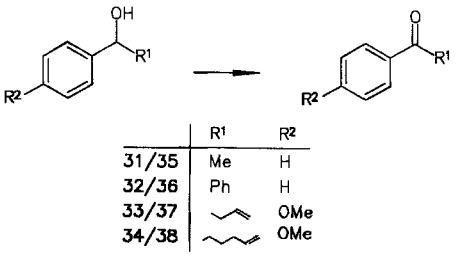
Figure 2. Yields of 3-methoxybenzaldehyde (**14**) and 4-nitrobenzaldehyde (**18**) in the $Ti(OiPr)_4$-catalyzed dehydrogenation of **3** and **7** (1 equiv. of TBHP)

It was known that transition metal complexes cause slow decomposition of TBHP, and therefore 1.5 equivalents of TBHP was used in the experiments shown in Table 1. The decomposition was confirmed by NMR experiments, which showed the slow formation of *tert*-butanol from TBHP in the presence of $Ti(OiPr)_4$. The exact amount of TBHP consumed was measured by titration of the TBHP remaining after quantitative conversion of benzyl alcohol (**1**) into benzaldehyde (**12**). It could be shown that a maximum of 10% TBHP was decomposed in the zirconium-catalyzed reactions after 24 h of reaction time.

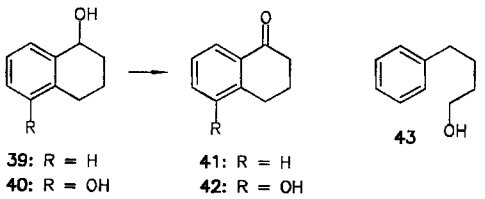
With the exception of the phenolic aldehydes **16** and **42**, which were filtered through a short column of silica gel, chromatographic purification of the products was *not* required. It could be shown that filtration of the reaction mixture through a short column of silica gel did *not* remove the transition metal catalyst completely. Workup can be effected either under neutral or slightly acidic conditions. Addition of water to the stirred dichloromethane solution hydrolyzed the metal complex. In small-scale reactions the resulting heterogeneous mixture can be dried by addition of sodium or magnesium sulfate and filtered. Alternatively, dilute sulfuric acid may be used for hydrolysis to obtain two transparent, well-separated phases. It is often not necessary to remove the remaining traces of TBHP in small-scale reactions (1 mmol) and when crystalline products are isolated. The method is amenable to scale-up, but then the well-established reduction procedures using sodium sulfite[19] or iron(II) sulfate[17] may be used to remove TBHP (for other reducing methods see ref.[19,20]).

In the next set of experiments the dehydrogenation of the secondary alcohols **31**–**34**, **39**, **40**, and **44** was studied. The conditions shown in Table 1 (entries 28–36) and the high yields indicate that the increased steric hindrance was easily

overcome by the inductive effect (vide infra) of the additional alkyl group. No attack on the double bond in **34** or even in the homoallylic alcohol **33** was observed in dehydrogenation to the ketones **38** and **37** in the zirconium-catalyzed reaction (entries 30, 31). By contrast, homoallylic alcohols are known to be slowly epoxidized by the $Ti(OiPr)_4$-, $VO(acac)_2$-[16], or $Zr(OnPr)_4$-catalyzed[21] reactions with TBHP.



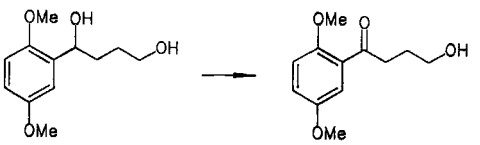
	R^1	R^2
31/35	Me	H
32/36	Ph	H
33/37	⟨	OMe
34/38	⟨	OMe



39: R = H
40: R = OH

41: R = H
42: R = OH

43



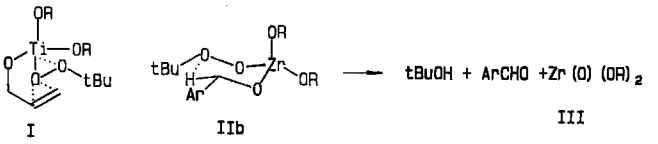
44 **45**

3-Phenyl-1-butanol (**43**) was just one of the many primary and secondary *non*-benzylic alcohols tested in the zirconium-catalyzed reaction which showed no reaction after 24 h. Compound **44** is an example in which a benzylic and a primary non-benzylic alcohol group are present in the same molecule. In the experiment (entry 36) the selective dehydrogenation of the benzylic hydroxy group to the hydroxy ketone **45** (89% yield) was observed, demonstrating the high chemoselectivity with respect to benzylic hydroxy groups in the zirconium-catalyzed dehydrogenation.

Mechanism

Much work has been performed in recent years on the transition-metal-mediated epoxidation of olefins[16], on the enantioselective epoxidation of allylic alcohols[17,22–24], and recently on the oxygenation of phenols to *ortho*-quinones[1]. The decisive oxygen transfer is believed to proceed by a dispiro transition state like **I**[22,25,26]. The titanium species perhaps occurs in a dimeric form[22,27].

In contrast to the oxygen transfer processes, little attention has been paid to transition-metal-catalyzed *dehydrogenation* with TBHP. A very few examples are mentioned in the literature, where dehydrogenation of allylic alcohols to unsaturated aldehydes has been observed as an undesired side reaction in epoxidation[28–30].



I **IIb** **III**

Exchange of the alcoholic ligands in the transition metal complexes is known to be very fast[16,22]. That the process is fast compared to the NMR time scale could be shown by the downfield shift of the benzylic protons in the ^{1}H-NMR spectrum when mixing $Ti(OiPr)_4$ and the benzyl alcohol **3**. The magnitude of the shift depended on the ratio of benzyl alcohol and metal complex, and no splitting of the protons in complexed and uncomplexed form could be seen (cf. the behavior of NMR shift reagents). The reactive transition metal complex **II** in which the hydrogen transfer occurs could be formed in two ways from **IV** or **V**, as shown in equations (1) and (2).

$$\underset{\mathbf{IV}}{Zr(OR)_3(OCH_2Ar)} + HOOtBu \rightarrow \underset{\mathbf{II}}{Zr(OR)_3(OCH_2Ar)(OOtBu)} + HOR \quad (1)$$

$$\underset{\mathbf{V}}{Zr(OR)_3(OOtBu)} + HOCH_2Ar \rightarrow \mathbf{II} + HOR \quad (2)$$

In contrast to the oxygen transfer, the dehydrogenation presumably requires a totally different transition state. This provides the chance of "decoupling" the oxygenation process from the dehydrogenation even if the activation of TBHP (by weakening the O–O bond) is similar. Teranishi et al. propose a five-membered transition state in the vanadium-catalyzed dehydrogenation of cyclic allylic axil alcohols, accompanied by a change in oxidation state of the transition metal[30]. We suggest the six-membered chair transition state **IIb** for the zirconium-catalyzed reactions, in which three of the four residues or ligands can assume a sterically favored equatorial position. The presence of dimeric or even oligomeric forms of the zirconium alcoholate[31] does not change the nature of the hydrogen transfer. In this model a partial positive charge is developed at the benzylic center during hydrogen transfer to TBHP. This is supported by the kinetic data of competition ^{1}H-NMR experiments between the electron-rich substrate **3** and electron-deficient 4-nitrobenzyl alcohol (**7**) using the $Ti(OiPr)_4$ catalyst (see Experimental, Tables 2 and 4). Figure 2 clearly illustrates the much faster (approximately four times as fast) conversion of donor-substituted 3-methoxybenzyl alcohol (**3**) compared with acceptor-substituted 4-nitrobenzyl alcohol (**7**), supporting the involvement of a positively charged transition state in the rate-determining step. Model considerations further show that the formation of an unhindered six-membered transition state such as **IIb** is prevented by chelated coordination of the substrates to the metal atom. This could explain the drastic decrease in reaction rates of the phenols **2** and **27** and pyridine **23**. The regeneration of $Zr(OR)_4$ from the oxozirconium dialcoholate **III** can occur by addition of alcohols present in the reaction mixture and elimination of water as shown in equation (3).

$$\mathbf{III} + 2\ ROH \rightarrow Zr(OR)_4 + H_2O \quad (3)$$

If the water is not removed by molecular sieves, a slow deactivation by hydration of the catalyst is observed. It is supposed that the hydration may form various condensed oligomeric forms of the zirconium complex (compare ref.[31,32]).

The results presented in this paper show unprecedented selectivity for a limited spectrum of applications. Investigations including aspects of asymmetric induction (kinetic resolution), more detailed mechanistic and kinetic studies, oxidation of primary alcohols to carboxylic acids and aliphatic secondary alcohols to ketones are under way and will be communicated in forthcoming papers.

Experimental

For general remarks see ref.[1]. The IR bands for the benzylic carbonyl groups were in the range of $\tilde{\nu}$ = 1665–1695 cm^{-1}.

General Procedure for the Dehydrogenation of Benzylic Alcohols with TBHP and Catalytic Amounts of Ti(OiPr)$_4$ or Zr(OnPr)$_4$: A solution of 1.0 mmol of benzylic alcohol in 10 ml of dry CH_2Cl_2 was stirred at 20°C under nitrogen with 200 mg of molecular sieves. After 10 min, 0.03 ml (0.1 mmol) of Ti(O*i*Pr)$_4$ or Zr(O*n*Pr)$_4$ and then 0.38 ml (1.5 mmol) of a 29.6% solution of TBHP in CH_2Cl_2 (for preparations of dry solutions of TBHP in CH_2Cl_2 see ref.[17]) were added with a syringe. The reactions were monitored by TLC (CH_2Cl_2) and worked up after the times indicated in Table 1. For workup under *neutral* conditions 1 ml of water was added, and the mixture stirred for 1 h. Then 3 g of Na_2SO_4 was added, stirring was continued for 10 min, and the mixture filtered and washed with CH_2Cl_2. The solvent and traces of TBHP were removed under reduced pressure (first ca. 50 and then 1 Torr) using two traps cooled with liquid nitrogen. For *acidic* workup the CH_2Cl_2 solution was stirred for 1 h with 10 ml of 10% sulfuric acid prior to drying and removal of the solvent. In larger scale reactions (Table 1, entry 2) the excess of TBHP was removed by vigorously stirring the mixture under nitrogen for 1 h with an aqueous solution of $FeSO_4$ (at least 30% excess of the theoretically necessary amount of $FeSO_4$). With acetone or THF as solvent, 30 ml of CH_2Cl_2 was added prior to workup. According to TLC most zirconium-catalyzed reactions proceeded quantitatively (exceptions: entries 3, 20, 21) and no chromatography was necessary for non-phenolic products. Remaining starting material from the titanium-catalyzed reactions was removed by filtration through a short (5 × 1 cm) column of silica gel (CH_2Cl_2 as eluent). Liquid products could be distilled by Kugelrohr distillation (entry 2) or crystallized from ether/petroleum ether (entries 8, 9, 15–31). Most simple aldehydes (**12–22, 24, 26**) and ketones (**35, 36, 41**) are well known, mostly commercially available compounds, and were identified from their ^{1}H-NMR spectra. The data of unknown or less well-known compounds are listed below. For yields, reaction times, and deviations in amounts of reactants or the kind of solvent see Table 1.

2-Hydroxymethyl-1,5-dimethoxy-9,10-anthraquinone (**28**): A solution of 564 mg (2 mmol) of 1-hydroxy-2-hydroxymethyl-5-methoxy-9,10-anthraquinone[33] in acetone was methylated with dimethyl sulfate in the presence of potassium carbonate (12 h, reflux) to afford 520 mg (87%) of **28**; m.p. 172°C. – UV (methanol): λ_{max} (lg ε) = 219 nm (4.53), 258 (4.58), 375 (sh), 388 (3.93), 419 (sh). – ^{1}H NMR (400 MHz): δ = 2.33 (t, *J* = 6.2 Hz; 1H, OH), 3.97 (s; 3H, OCH_3), 4.05 (s; 3H, OCH_3), 4.86 (d, *J* = 6.2 Hz; 2H, CH_2OH), 7.31 (dd, $J_{6,7}$ = 8.0, $J_{6,8}$ = 0.8 Hz; 1H, 6-H), 7.72 (t, $J_{6,7}$ = $J_{7,8}$ = 8.0 Hz; 1H, 7-H), 7.83 (d, *J* = 7.9 Hz; 1H, 3- or 4-H), 7.90 (dd, $J_{7,8}$ = 8.0, $J_{6,8}$ = 0.8 Hz; 1H, 8-H), 8.09 (d, *J* = 7.9 Hz; 1H, 4- or 3-H). – ^{13}C NMR (100 MHz): δ = 56.58 (prim.), 60.77 (sec.), 62.20 (prim.), 117.25 (tert.), 119.71 (tert.), 120.97 (quat.), 123.72 (tert.), 124.70 (quat.), 133.84 (tert.), 135.15 (tert.), 136.55 (quat.), 137.08 (quat.), 141.33 (quat.), 157.89 (quat.), 159.94 (quat.), 182.26 (quat.), 182.80 (quat.). – MS (120°C): *m/z* (%) = 298 (43) [M^+], 283 (100) [$M^+ - CH_3$], 268 (59) [$M^+ - CH_2O$], 267 (32) [$M^+ - CH_2OH$], 253 (43), 237 (44), 223 (35), 209 (32), 206 (16), 181 (22), 165 (30), 152 (32), 139 (25).

$C_{17}H_{14}O_5$ (298.3) Calcd. C 68.45 H 4.73
Found C 68.41 H 4.70

2-Formyl-1-hydroxy-5-methoxy-9,10-anthraquinone (**29**): A solution of 1 mmol of 1-hydroxy-2-hydroxymethyl-5-methoxy-9,10-anthraquinone[33] in CH_2Cl_2 was treated as described in the general procedure using Ti(O*i*Pr)$_4$ to afford 118 mg (42%) of **29**, yellow crystals, m.p. 193°C (diethyl ether). – UV (methanol): λ_{max} (lg ε) = 205 nm (sh), 226 (4.47), 246 (sh), 411 (3.89). – ^{1}H NMR (400 MHz): δ = 4.08 (s; 3H, OCH_3), 7.42 (dd, $J_{6,7}$ = 8.1, $J_{6,8}$ = 0.9 Hz; 1H, 6-H), 7.80 (t, $J_{6,7}$ = $J_{7,8}$ = 8.1 Hz; 1H, 7-H), 7.85 (d, *J* = 7.9 Hz; 1H, 4- or 3-H), 8.01 (dd, $J_{7,8}$ = 8.1, $J_{6,8}$ = 0.9 Hz; 1H, 8-H), 8.22 (d, *J* = 7.9 Hz; 1H, 3- or 4-H), 10.61 (s; 1H, CHO), 13.08 (s; 1H, OH). – ^{13}C NMR (100 MHz): δ = 56.70 (prim.), 116.88 (quat.), 118.62 (tert.), 119.10 (tert.), 119.71 (tert.), 127.46 (quat.), 135.03 (quat.), 135.57 (tert.), 135.64 (tert.), 138.86 (quat.), 160.80 (quat.), 164.09 (quat.), 171.19 (quat.), 188.00 (tert.), 188.00 (quat.), 188.87 (quat.). – MS (100°C): *m/z* (%) = 282 (47) [M^+], 254 (100) [$M^+ - CO$], 225 (15) [$M^+ - CO - CHO$], 208 (9), 197 (10), 168 (12), 139 (21).

$C_{16}H_{10}O_5$ (282.2) Calcd. C 67.60 H 3.54
Found C 67.46 H 3.95

2-Formyl-1,5-dimethoxy-9,10-anthraquinone (**30**): A solution of 298 mg (1 mmol) of 2-hydroxymethyl-1,5-dimethoxy-9,10-anthraquinone (**28**) was treated as described in the general procedure using Zr(O*n*Pr)$_4$ to afford 287 mg (97%) of **30**; light yellow crystals, m.p. 201°C. – UV (methanol): λ_{max} (lg ε) = 221 nm (4.44), 245 (sh), 256 (4.37), 270 (sh), 379 (3.82), 397 (3.83). – ^{1}H NMR (400 MHz): δ = 4.07 (s; 3H, OCH_3), 4.11 (s; 3H, OCH_3), 7.35 (dd, $J_{6,7}$ = 8.0, $J_{6,8}$ = 0.9 Hz; 1H, 6-H), 7.77 (t, $J_{6,7}$ = $J_{7,8}$ = 8.0 Hz; 1H, 7-H), 7.93 (dd, $J_{7,8}$ = 8.0, $J_{6,8}$ = 0.9 Hz; 1H, 8-H), 8.17 (dd, $J_{3,4}$ = 7.8, $J_{3,formyl\text{-}H}$ = 0.7 Hz; 1H, 3-H), 8.22 (d, $J_{3,4}$ = 7.8 Hz; 1H, 4-H), 10.57 (d, $J_{3,formyl\text{-}H}$ = 0.7 Hz; 1H, CHO). – ^{13}C NMR (100 MHz): δ = 56.64 (prim.), 64.66 (prim.), 117.50 (tert.), 119.79 (tert.), 120.73 (quat.), 123.47 (tert.), 126.03 (quat.), 133.45 (tert.), 133.65 (quat.), 135.67 (tert.), 136.88 (quat.), 141.11 (quat.), 160.14 (quat.), 163.36 (quat.), 181.53 (quat.), 182.11 (quat.), 189.08 (tert.). – MS (125°C): *m/z* (%) = 296 (100) [M^+], 281 (9) [$M^+ - CH_3$], 249 (19), 237 (25), 209 (18), 181 (14), 152 (23), 151 (19).

$C_{17}H_{12}O_5$ (296.3) Calcd. C 68.91 H 4.08
Found C 69.04 H 4.07

1-(4-Methoxyphenyl)-3-buten-1-ol (**33**): The procedure of Wilson and Guazzaroni[34] was employed for the preparation of **33**. A mixture of 1.36 g (10 mmol) of 4-methoxybenzaldehyde, 10 ml of a satd. aqueous solution of ammonium chloride, 2 ml of THF, 2.42 g (20 mmol) of allyl bromide and 1.31 g (20 mmol) of zinc dust was stirred for 1 h at room temp. The mixture was extracted twice with 100 ml of ether, and the organic phase dried with $MgSO_4$. The solution was filtered and the solvent removed at reduced pressure to afford 1.57 g (88%) of alcohol **33**[35]. – UV (methanol): λ_{max} (lg ε) = 207 nm (3.75), 226 (4.11), 276 (3.27), 282 (3.20). – ^{1}H NMR (400 MHz): δ = 2.34 (s; 1H, OH), 2.47 (m; 2H, CH_2), 3.77 (s; 3H, OCH_3), 4.63 (t, $J_{1,2}$ = 6.5 Hz; 1H, 1-H), 5.08–5.14 (m; 2H, 4-H), 5.71–5.81 (m; 1H, 3-H), 6.83–6.87 (m; 2H, Ar-H), 7.22–7.25 (m; 2H, Ar-H). – ^{13}C NMR (400 MHz): δ = 43.68 (sec.), 55.29 (prim.), 73.01 (tert.), 113.76 (tert., 2C), 118.02 (sec.), 127.10 (tert., 2C), 134.67

(tert.), 136.14 (quat.), 158.97 (quat.). – MS: *m/z* (%) = 178 (1) [M^+], 137 (100) [$M^+ - C_3H_5$], 135 (17), 109 (44), 77 (31).

$C_{11}H_{14}O_2$ (178.2) Calcd. C 74.12 H 7.91
Found C 73.86 H 7.93

1-(4-Methoxyphenyl)-5-hexen-1-ol (**34**): A Grignard reagent was prepared by the usual method from 0.97 g (0.04 mol) of magnesium and 5.96 g (0.04 mol) of 5-bromo-1-pentene in 50 ml of dry ether. A solution of 4.35 g (0.03 mol) of 4-methoxybenzaldehyde in 50 ml of dry ether was added within 30 min and the mixture heated for 2 h at reflux. A cold, satd., aqueous solution of ammonium chloride was added until the precipitate initially formed redissolved to a clear solution. The two phases were separated, and the aqueous phase was extracted twice with 50 ml of ether. The combined organic phases were washed with solutions of sodium hydrogen sulfite, sodium hydrogen carbonate, and water. The combined organic phases were dried with Na_2SO_4, the solvent was removed under reduced pressure and the residue distilled at 1 Torr to afford 4.81 g (73%) of **34**. – UV (methanol): λ_{max} (lg ε) = 209 nm (sh), 226 (4.07), 276 (3.24), 282 (3.17). – ^{1}H NMR (400 MHz): δ = 1.21–1.32 (m; 1H), 1.37–1.48 (m; 1H), 1.55–1.64 (m; 1H), 1.66–1.75 (m; 1H), 1.97–2.03 (m; 1H), 3.32 (s; 1H, OH), 3.70 (s; 3H, OCH_3), 4.47 (t, $J_{1,2}$ = 6.7 Hz; 1H, 1-H), 4.89–4.98 (m; 2H, 6-H), 5.68–5.78 (m; 1H, 5-H), 6.77–6.81 (m; 2H, Ar-H), 7.14–7.18 (m; 2H, Ar-H). – ^{13}C NMR (100 MHz): δ = 25.76 (sec.), 34.24 (sec.), 39.09 (sec.), 55.69 (prim.), 74.35 (tert.), 114.27 (tert., 2C), 115.14 (sec.), 127.76 (tert., 2C), 137.90 (quat.), 139.29 (tert.), 159.42 (quat.). – MS: *m/z* (%) = 205 (0.03) [$M^+ - H$], 188 (1) [$M^+ - H_2O$], 147 (41), 134 (6), 115 (11), 91 (18), 86 (22), 84 (34), 74 (56), 68 (19), 67 (27), 59 (100).

$C_{13}H_{18}O_2$ (206.3) Calcd. C 75.69 H 8.79
Found C 75.89 H 8.86

1-(4-Methoxyphenyl)-3-buten-1-one (**37**): A solution of 178 mg (1 mmol) of **33** in 10 ml of CH_2Cl_2 was treated with 0.38 ml (1.5 mmol) of 29.6% TBHP and 0.06 ml (0.2 mmol) of $Zr(OnPr)_4$ as described in the general procedure, to afford 161 mg (92%) of **37**; m.p. 41°C. – UV (methanol): λ_{max} (lg ε) = 207 nm (sh), 218 (4.09), 274 (4.25). – ^{1}H NMR (400 MHz): δ = 3.70–3.73 (m; 2H, 2-H), 3.87 (s; 3H, OCH_3), 5.18–5.24 (m; 2H, 4-H), 6.03–6.14 (m; 1H, 3-H), 6.95 (m; 2H, Ar-H), 7.94–7.97 (m; 2H, Ar-H). – ^{13}C NMR (100 MHz): δ = 43.25 (sec.), 55.48 (prim.), 113.78 (tert., 2C), 118.47 (sec.), 130.61 (tert., 2C), 130.67 (quat.), 131.47 (tert.), 163.56 (quat.), 196.62 (quat.). – MS (80°C): *m/z* (%) = 176 (7) [M^+], 135 (100) [$M^+ - C_3H_5$], 107 (16) [$M^+ - C_3H_5CO$], 92 (21) [$M^+ - C_3H_8CO - CH_3$], 77 (30), 64 (14), 63 (11).

$C_{11}H_{12}O_2$ (176.2) Calcd. C 74.97 H 6.86
Found C 74.69 H 6.92

1-(4-Methoxyphenyl)-5-hexen-1-one (**38**): A solution of 206 mg (1 mmol) of **34** was converted into 195 mg (96%) of **38** as described in the general procedure. – UV (methanol): λ_{max} (lg ε) = 208 nm (sh), 218 (4.07), 272 (4.23). – ^{1}H NMR (400 MHz): δ = 1.80–1.87 (m; 2H, CH_2), 2.12–2.18 (m; 2H, CH_2), 2.91 (t, *J* = 7.4 Hz; 2H, 2-H), 3.86 (s; 3H, OCH_3), 4.98–5.07 (m; 2H, 6-H), 5.77–5.87 (m; 1H, 5-H), 6.91–6.94 (m; 2H, Ar-H), 7.92–7.96 (m; 2H, Ar-H). – ^{13}C NMR (100 MHz): δ = 23.56 (sec.), 33.27 (sec.), 37.38 (sec.), 55.44 (prim.), 113.68 (tert., 2C), 115.21 (sec.), 130.17 (quat.), 130.29 (tert., 2C), 138.15 (tert.), 163.36 (quat.), 198.84 (quat.). – MS: *m/z* (%) = 204 (10) [M^+], 150 (77), 135 (100) [$M^+ - C_5H_9$], 107 (15), 92 (19), 77 (28).

$C_{13}H_{16}O_2$ (204.3) Calcd. C 76.44 H 7.89
Found C 76.34 H 8.02

5-Hydroxy-1-tetralone (**42**): A solution of 164 mg (1 mmol) of commercially available 1,5-dihydroxy-1,2,3,4-tetrahydronaphthalene (**40**) in 10 ml of CH_2Cl_2 was treated as described in the general procedure using $Zr(OnPr)_4$, to afford 156 mg (96%) of light yellow **42**; m.p. 206°C (ether) (ref.[36] 210–211.5°C). – ^{1}H NMR (400 MHz): δ = 2.12–2.19 (m; 2H), 2.64–2.67 (m; 2H), 2.90 (t, *J* = 6.2 Hz; 2H), 5.17 (s; 1H, OH), 6.98 (dd, *J* = 7.9, *J* = 1.0 Hz; 1H), 7.18 (t, *J* = 7.9 Hz; 1H), 7.66 (dd; *J* = 7.9, *J* = 1.0 Hz; 1H). – MS: *m/z* (%) = 162 (100) [M^+], 147 (26), 134 (88) [$M^+ - CO$], 120 (13), 106 (63), 91 (9).

1-(2,5-Dimethoxyphenyl)-1,4-butanediol (**44**): A suspension of 2.38 g (10 mmol) of 4-(2,5-dimethoxyphenyl)-4-oxobutanoic acid[37] in 10 ml of ether was slowly added to a suspension of 0.34 g (8.6 mmol) of $LiAlH_4$ (LAH) in 10 ml of dry ether. The mixture was then heated at reflux for 30 min and hydrolyzed by careful addition of 1 ml of a 10% solution of sodium hydrogen carbonate and 2 ml of 20% NaOH. The organic phase was decanted and the aqueous solution washed three times with 5 ml of ether. The combined organic phases were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The residue was separated from unreacted polar material by filtration through silica gel (eluent CH_2Cl_2/10% ether) to afford 0.81 g (36%) of **44**; m.p. 56°C. – UV (methanol): λ_{max} (lg ε) = 206 nm (4.00), 227 (3.90), 291 (3.58). – ^{1}H NMR (400 MHz): δ = 1.62–2.00 (m; 4H), 3.40 (br. s; 2H, 2 OH), 3.60–3.66 (m; 2H, CH_2), 3.74 (s; 3H, OCH_3), 3.77 (s; 3H, OCH_3), 4.88–4.91 (m; 1H, 1-H), 6.71–6.78 (m; 2H, Ar-H), 6.96 (d, *J* = 2.9 Hz; 1H, Ar-H). – ^{13}C NMR (100 MHz): δ = 29.38 (sec.), 34.46 (sec., 2C), 55.71 (prim.), 55.84 (prim.), 62.74 (sec.), 111.45 (tert.), 112.40 (tert.), 112.83 (tert.), 133.93 (quat.), 150.39 (quat.), 153.72 (quat.). – MS (35°C): *m/z* (%) = 226 (23) [M^+], 167 (100) [$M^+ - C_3H_6OH$], 152 (16), 151 (7), 139 (57), 137 (31), 124 (26).

$C_{12}H_{18}O_4$ (226.3) Calcd. C 63.69 H 8.01
Found C 63.42 H 8.04

1-(2,5-Dimethoxyphenyl)-4-hydroxy-1-butanone (**45**): A solution of 226 mg (1 mmol) of **44** was converted into 198 mg (86%) of **45** as described in the general procedure [catalyst 0.03 ml of $Zr(OnPr)_4$; 1.5 mmol of TBHP]. – UV (methanol): λ_{max} (lg ε) = 219 nm (4.41), 247 (3.68), 307 (sh), 331 (3.50). – ^{1}H NMR (400 MHz): δ = 1.93–1.99 (m; 2H, 3-H), 2.29 (br. s; 1H, OH), 3.11 (t, *J* = 6.9 Hz; 2H, 4-H), 3.70 (t, *J* = 6.2 Hz; 2H, 2-H), 3.79 (s; 3H, OCH_3), 3.86 (s; 3H, OCH_3), 6.91 (d, $J_{3',4'}$ = 9.0 Hz; 1H, 3′-H), 7.02 (dd; $J_{3',4'}$ = 9.0 Hz, $J_{4',6'}$ = 3.2 Hz; 1H, 4′-H), 7.25 (d, *J* = 3.2 Hz, 1H, 6′-H). – ^{13}C NMR (100 MHz): δ = 27.75 (sec.), 41.00 (sec.), 56.26 (prim.), 56.52 (prim.), 62.95 (sec.), 113.61 (tert.), 114.42 (tert.), 120.43 (tert.), 128.90 (quat.), 153.56 (quat.), 153.92 (quat.), 203.01 (quat.). – MS: *m/z* (%) = 224 (19) [M^+], 207 (6) [$M^+ - OH$], 206 (12) [$M^+ - H_2O$], 180 (22), 165 (100) [$M^+ - C_3H_6OH$], 150 (9), 135 (14), 122 (9), 97 (11), 87 (20), 75 (21), 57 (61).

$C_{12}H_{16}O_4$ (224.2) Calcd. C 64.27 H 7.18
Found C 64.10 H 7.25

Table 2. Dehydrogenation of **3** and **7** to afford **14** and **18** in the presence of 2 equiv. of TBHP and 0.2 mmol of $Ti(OiPr)_4$

Entry	*t* [h]	**14** (%)	**18** (%)
1	1.5	18.0	6.7
2	2.5	21.3	6.8
3	3.5	30.9	8.4
4	4.5	42.3	9.5
5	5.5	43.1	9.7
6	6.5	45.3	15.5
7	9.5	58	16.5
8	24	83.3	28.2

Kinetic Experiments. — Competition NMR Experiments: A mixture of 2.0 mmol of 3-methoxybenzyl alcohol (**3**), 2.0 mmol of 4-nitrobenzyl alcohol (**7**), 4.0 mmol of TBHP, 0.2 mmol of $Ti(OiPr)_4$, and 300 mg of molecular sieves (3 Å, Aldrich) in 10 ml of $CDCl_3$ was stirred under nitrogen. The reaction was monitored by ^1H-NMR spectroscopy (60 MHz, 23°C), taking 0.4 ml aliquots. The intensities of the signals for the methoxy groups of **3** and **7** and the respective aldehyde protons of **14** and **18** were measured at constant time intervals. The values are shown in Table 2 and plotted in Figure 2.

A similar kinetic competition experiment was run with 3,4-methylenedioxybenzyl alcohol and 4-nitrobenzyl alcohol (**7**). The temperature was held at 40°C and 1.5 equiv. of TBHP per mol of alcohol was used (Table 3).

Table 3. Dehydrogenation of 3,4-methylenedioxybenzyl alcohol and 4-nitrobenzyl alcohol (**7**) in the presence of 3 equiv. of TBHP and 0.2 mmol of $Ti(OiPr)_4$

Entry	*t* [h]	3,4-Methylenedioxybenzaldehyde (%)	**18** (%)
1	0.5	33	5
2	1	60	8
3	2	63.5	9.2
4	3	64.7	13.2
5	4	65.6	15.6
6	5	67	17
7	22	70.6	22

In a third kinetic experiment 2.0 mmol of **3** in 5 ml of $CDCl_3$ was treated with 150 mg of molecular sieves, 0.2 mmol of $Zr(OnPr)_4$, and 1.0 mmol of TBHP and the reaction monitored by ^1H NMR (60 MHz, Table 4). Figure 1 shows the plot of these values against the conversion of the same substrate with $Ti(OiPr)_4$.

Table 4. Dehydrogenation of 3-methoxybenzyl alcohol (**3**) with 1 equiv. of TBHP and 0.1 mmol of $Zr(OnPr)_4$

Entry	*t* [h]	**14** (%)
1	0.25	31
2	0.5	41.5
3	1	60.7
4	2.83	86
5	4.33	92

Table 5. Simultaneous formation of aldehyde **14** and acetone in the titanium-catalyzed dehydrogenation of **3**

Entry	*t* [h]	**14** (%)	Acetone (%)
1	0.5	18.2	4.5
2	1	23	5.6
3	2	27	6.5
4	3	30.6	7.6
5	5	32.6	8.1
6	6	38.5	8.8
7	24	72	16

In a fourth experiment, the formation of acetone was simultaneously measured (400-MHz NMR) with the concentration of 3-methoxybenzaldehyde in the titanium-catalyzed reaction, as described above [1.0 mmol of **3**, 1.0 mmol of TBHP, 0.1 mmol of $Ti(OiPr)_4$, molecular sieves].

CAS Registry Numbers

1: 100-51-6 / **2**: 90-01-7 / **3**: 6971-51-3 / **4**: 456-47-3 / **5**: 623-05-2 / **6**: 105-13-5 / **7**: 619-73-8 / **8**: 873-76-7 / **9**: 7314-44-5 / **10**: 33524-31-1 / **11**: 16700-55-3 / **12**: 100-52-7 / **13**: 90-02-8 / **14**: 591-31-1 / **15**: 456-48-4 / **16**: 123-08-0 / **17**: 123-11-5 / **18**: 555-16-8 / **19**: 104-88-1 / **20**: 613-45-6 / **21**: 93-02-7 / **22**: 3392-97-0 / **23**: 586-95-8 / **24**: 872-85-5 / **25**: 4780-79-4 / **26**: 66-77-3 / **27**: 103576-79-2 / **28**: 125379-54-6 / **29**: 116161-92-3 / **30**: 125379-55-7 / **31**: 98-85-1 / **32**: 91-01-0 / **33**: 24165-60-4 / **34**: 71434-56-5 / **35**: 98-86-2 / **36**: 119-61-9 / **37**: 85234-21-5 / **38**: 125379-56-8 / **39**: 529-33-9 / **40**: 40771-26-4 / **41**: 529-34-0 / **42**: 28315-93-7 / **44**: 125379-57-9 / **45**: 125379-58-0 / $Ti(OiPr)_4$: 546-68-9 / $Zr(OnPr)_4$: 23519-77-9 / $VO(acac)_2$: 3153-26-2 / 4-methoxybenzaldehyde: 123-11-5 / 4-(2,5-dimethoxyphenyl)-4-oxobutanoic acid: 1084-74-8

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[391/89]