Concerning chemistry, reactivity, and mechanism of transition metal catalysed oxidation of benzylic compounds by means of ozone

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Abstract

Chemistry, reactivity, and mechanism of transition metal catalysed oxidation of benzylic compounds by means of ozone were systematically investigated. A significant influence of substituents on the reactivity of the benzylic position correlating with the Hammett coefficients of these substituents as well as with their steric influences was observed. It was shown, that mono-oxidation of compounds with different benzylic groups is possible in high regioselectivity and that the reaction seems to proceed via a mechanism including radical species.
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1. Introduction

Benzylic oxidations are extensively used in the syntheses of fine or speciality chemicals. The majority of the processes employed industrially involves catalysis by various metal complexes [1], and an increasing variety of catalytic processes have been developed over the last years [2]. Catalytic processes enjoy the advantages over their non-catalytic counterparts of proceeding efficiently under mild energy efficient conditions [3], higher selectivity, and they do not produce vast amounts of inorganic effluents like traditional oxidants (e.g. MnO_4^- or $Cr_2O_7^{2-}$). Thus, a greater emphasis has to be placed on the development of new, improved catalytic processes.

Although known for a long time, only a limited number of different oxidative transformations involving ozone, mainly the selective cleavage of double bonds, have been applied [4]. Ozonisation in combination with catalysts is generally used in wastewater treatment [5], but only few examples of organic oxidations by means of ozone in the presence of a transition metal catalyst are reported. In 1991, Meunier and co-workers [6] and recently Griffith and co-workers [7] reported the use of an O_3–O_2 mixture to epoxidise alkenes under ambient conditions, but with low selectivity and low catalyst turnover numbers, due to the decomposition of the used porphyrin ligands by ozone. Gross and co-workers [8,9] have investigated the hydroxylation of ethyl benzene effected by ozone in the presence of porphyrin complexes and Neumann and Khenkin [10] have studied alkane oxidations catalysed by the polyoxometalate $Li_{12}[Mn_2ZnW(ZnW_9O_{34})_2]$ with ozone as the preliminary oxidant.

We have recently found that the combined use of Mn(II) acetate and ozone results in an industrially attractive and very powerful process for the preparation of substituted benzaldehydes [11] and substituted benzoic acids [12] under ambient conditions without any toxic off-gas emission related to other methods (e.g. HNO_3 oxidations). The only off-gas produced is oxygen which can be recycled for the generation of ozone. This method is superior to others as the oxidation of toluene derivatives can be directed either towards the aldehyde or the carboxylic acid as the main product, by a proper choice of the reaction conditions and selection of different solvents. If the aldehyde is the desired product, the reaction is performed in acetic anhydride and primarily yields the acylal,

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Scheme 1. Manganese(II) catalysed oxidation of toluene derivatives by means of ozone.

which can be subsequently hydrolysed to the free aldehyde (Scheme 1). Thus, any over-oxidation to the carboxylic acid can be avoided.

To make use of this method, it is necessary to attain knowledge about the influence of substituents on the reactivity of benzylic compounds with respect to their electronic properties as well as with respect to possible steric influences on the reaction centre. Furthermore, information about the reactivity of different benzylic groups and a possible reaction mechanism of this new type of reaction are of major interest. Following this quest, we have now systematically investigated chemistry, reactivity, and mechanism of this type of reaction as well as the usefulness of this method in selective oxidation of compounds with different benzylic groups.

2. Experimental

All chemicals and reagents were obtained from commercial suppliers and used without purification prior to use, except otherwise stated. NMR spectra were recorded on a Bruker DRX-300 at 300 MHz for ^{1}H NMR spectra and 75 MHz for ^{13}C NMR spectra. GC–MS spectra were recorded on a Hewlett-Packard HP6890 series II gas chromatograph using a HP-5MS column (30 m × 0.32 mm × 0.25 μm) coupled to a HP5971A mass spectrometer. Analyses of acidic compounds (benzoic acids, alcohols) were carried out with BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide) as a derivatization reagent (silylation of acidic function).

2.1. Apparatus

Reactions were carried out in a jacketed and cooled batch reactor ("Schmizo"). Ozone was generated by an air-cooled BMT 803 generator, operated at a flow of $0.165 \, m^3 \, O_2 \, h^{-1}$ and introduced into to the reaction vessel by a glass tube bearing a medium porosity frit. Ozone uptake of the reaction solution was determined by comparing the ozone concentrations of feed- and off-gas. Ozone concentration was monitored by means of a Fischer OZOTRON 23 using UV–vis-spectroscopy.

2.2. General procedures

2.2.1. Method A

2.0 g substrate, 0.5 equivalents H_2SO_4, and 0.005 equivalents Mn(II) acetate were dissolved in 200 cm^3 AcOH, in-

troduced into the reactor, homogenised, and cooled to 20 °C. Two equivalents O_3 were introduced with a constant stream of $0.165 \, m^3 \, O_2 \, h^{-1}$ and a typical O_3 amount of $20 \, g \, h^{-1} \, m^{-3}$. After determination of the peroxide concentration by iodometry and reduction of the peroxides with a reducing agent (dimethylsulfide), the reaction solution was extracted with CH_2Cl_2/H_2O for three times. Combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The products were identified by comparison with reference materials.

2.2.2. Method B

2.0 g starting material, 0.5 equivalents H_2SO_4, and 0.005 equivalents Mn(II) acetate were dissolved in 200 cm^3 Ac_2O, introduced into the reactor, homogenised, and cooled to 20 °C. One equivalent O_3 was introduced with a constant stream of $0.165 \, m^3 \, O_2 \, h \, h^{-1}$ and a typical O_3 amount of $20 \, g \, h^{-1} \, m^{-3}$. After reduction of peroxides, the solution was hydrolysed after addition of 200 cm^3 water (90 °C) for at least 90 min and extracted with CH_2Cl_2/H_2O for three times. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated. The products were identified by comparison with reference materials.

Oxidation of *N,N*–dimethyl-*p*-toluidine (**1**): Method A gave only unidentified cleavage products.

Oxidation of 4-methylanisole (**2**): Method A without sulfuric acid and addition of three equivalents O_3 gave 95% *p*-anisic acid (**28**) in 70% yield. Products were analysed by GC–MS, ^{1}H NMR, and ^{13}C NMR. Retention time and mass spectra were identical with those of the reference. Method B without sulfuric acid gave total conversion of starting material to rearrangement products, but no selective oxidation. NMR spectra were identical with the literature spectra [13].

Oxidation of 4-*tert*-butyltoluene (**3**): Method A with Mn(III) acetate gave total conversion, yielding 4-*tert*-butylbenzoic acid (**29**) with 95% selectivity in 80% yield. Method B with Mn(III) acetate gave total conversion to 4-*tert*-butylbenzaldehyde (**30**) with 94% selectivity in 80% yield. Products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

Oxidation of *p*-xylene (**4**): Method A gave total conversion, yielding *p*-tolylic acid (**10**) with 95% selectivity. Method B gave total conversion, yielding *p*-tolualdehyde (**11**) with 70%, and 4-methyl-benzylacetate (**12**) with 28% selectivity. Products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

Oxidation of 4-bromotoluene (**5**): Method A gave total conversion to *p*-bromobenzoic acid (**31**) in 70% yield. Method B gave total conversion of **5** to yield 4-bromobenzaldehyde (**32**) with over 90% selectivity in 60% yield. Products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

Oxidation of methyl-3-methyl benzoate (**6**): Method A, adding three equivalents O_3 and using a catalyst system consisting of 0.8 equivalents H_2SO_4 and 0.02 equivalents Mn(II) acetate, gave 33% conversion to mono methyl-isophthalic acid (**33**). The product was analysed by GC–MS. Retention time and mass spectrum was identical with those of a reference.

Oxidation of 3-bromotoluene (**7**): Method A, adding three equivalents O_3 and using a catalyst system consisting of 0.75 equivalents H_2SO_4 and 0.0075 equivalents Mn(II) acetate, gave total conversion to 3-bromobenzoic acid (**34**). Method B, adding 1.5 equivalents O_3 and using a catalyst system consisting of 0.75 equivalents H_2SO_4 and 0.0075 equivalents Mn(II) acetate, gave total conversion, yielding 3-bromobenzaldehyde (**35**) with 70% selectivity. The products were analysed by GC–MS. Retention times and mass spectra were identical with those of the references.

Oxidation of 4-methylacetophenone (**8**): Method A gave 8% conversion. *p*-Acetylbenzoic acid (**36**) was obtained with 99% selectivity. Product was analysed by GC–MS. Retention time and mass spectrum was identical with those of a reference.

Oxidation of 3-tolunitrile (**9**): Neither Method A, nor Method B gave any conversion.

Oxidation of 2-bromotoluene (**13**): Method A, adding three equivalents O_3 and using a catalyst system consisting of 0.75 equivalents H_2SO_4 and 0.0075 equivalents Mn(II) acetate, gave 75% conversion. 2-Bromobenzoic acid (**14**) was obtained with nearly 70% and 2,4-dibromotoluene (**15**) with about 20% selectivity. Products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

Oxidation of mesitylene (**16**): Method A gave 90% conversion, yielding 3,5-dimethylbenzaldehyde (**17**) with 40% and 3,5-dimethylbenzoic acid (**18**) with 25% selectivity. The residue was dissolved in 150 cm^3 acetic acid, one equivalent

H_2O_2 was added, heated to 60 °C, and stirred for 1.5 h. Reaction solution was worked up as usual, giving a total conversion of **17–18** with an overall yield of about 65%. The products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

Oxidation of *m*-ethyltoluene (**19**): Method A gave total conversion of **18**, giving 3-methylacetophenone (**20**) with over 70% selectivity and 3-ethylbenzoic acid (**21**) with about 25% selectivity. Method A, using a catalyst system consisting of 0.05 equivalents Mn(II) acetate and 0.05 equivalents sulfuric acid, gave total conversion, yielding **20** with over 50% selectivity, **21** with about 35%. The products were analysed by GC–MS and ^{1}H NMR and ^{13}C NMR. Retention times and mass spectra were identical with those of references. NMR spectra were identical with the literature spectra [13].

Oxidation of *p*-cymene (**22**): Method A gave 85% conversion. 4-Methylacetophenone **8** was obtained with nearly 70% selectivity, 4-*i*-propylbenzoic acid (**23**) with less than 25%. The products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

Oxidation of methyl-4-tolylacetate (**24**): The substrate **24** had to be prepared by esterification of the commercially available 4-methyl-phenylacetic acid (**37**) [14]. Method A gave less than 25% conversion. Methyl-(4-carboxy)phenylacetate (**25**) was obtained with 50% selectivity, *p*-tolylic acid (**10**) with 15%, methyl-(4-methyl)benzoylformate (**26**) with 6%, and 4-methyl-benzyl alcohol (**27**) with 15%. Products were analysed by GC–MS. Retention times and mass spectra were identical with those of references.

3. Results and discussion

3.1. Electronic influence of substituents

With respect to the influence of various substituents on the reactivity of the benzylic position towards an oxidative attack, we investigated the dependence of this type of reaction on the nature of the substituent present on the aromatic moiety. Many detailed linear relationships between substituent groups and chemical properties have been developed to date [15], where the most widely applied is the Ham-

Table 1

Oxidation of selected toluene derivatives by O_3/Mn(II) in AcOH and/or Ac_2O and the Hammett coefficients (σ) of their substituents [20]

Compound	σ	Solvent	Conversion (%)	Comment
N,*N*-Dimethyl-*p*-toluidine (**1**)	−0.830	AcOH	100	Cleavage
4-Methylanisole (**2**)	−0.268	AcOH	100	Mild condition/$3O_3$
		Ac_2O	100	Rearrangement
4-*tert*-Butyltoluene (**3**)	−0.197	AcOH/Ac_2O	100	Mn(III) acetate
p-Xylene (**4**)	−0.170	AcOH/Ac_2O	100	Monooxidation
4-Bromotoluene (**5**)	0.232	AcOH/Ac_2O	100	–
Methyl-3-methyl benzoate (**6**)	0.330	AcOH	36	Strong condition/$3O_3$
3-Bromotoluene (**7**)	0.391	AcOH/Ac_2O	100	Strong condition
4-Methylacetophenone (**8**)	0.502	AcOH	8	–
		Ac_2O	0	–
3-Tolunitrile (**9**)	0.560	AcOH/Ac_2O	0	–

mett equation [16]. It is commonly used for the description of reactions, involving ionic structures of the transition state. However, Zavitsas et al. [17] showed that Hammett correlations can also be used to describe non-ionic reactions, which might make them useful to investigate reactions like benzylic oxidations.

All toluene derivatives were oxidised under the same conditions (exceptions will be mentioned) and we found, that the conversion rate widely changes with the substituent. Results obtained for acetic anhydride as the reaction medium (with the corresponding benzaldehyde as the desired product) are in most cases quite similar to those obtained for acetic acid (Table 1).

As expected, compounds with negative Hammett coefficients of its substituents turned out to be very reactive towards an oxidative attack. However, selective oxidation of the highly activated dimethylamino derivative **1** in AcOH was not possible due to the high electron density at the aromatic ring, which was cleaved under the reaction conditions. Moderately activated compounds, such as **2**, **3**, and **4** showed high conversion and high selectivity, whereas reaction of **2** in AcOH required a softer catalyst system (but then addition of three equivalents ozone) to avoid oxidative cleavage of the aromatic system. Selective oxidation of **2** in acetic anhydride was not possible due to the rearrangement of the anisole to yield acylated polyalkyl phenols. This can be explained by the fact that sulfuric acid–acetic acid mixtures [18] as well as Lewis acids [19] catalyse these rearrangements. The acylation of the oxygen function led to a deactivation of the methyl groups towards an oxidative attack and thus oxidation of the benzylic group was not possible any longer. Oxidation of **3** was the only experiment carried out in which a Mn(III) acetate-based catalyst system turned out to be more effective than the Mn(II)-based standard catalyst system.

Substrate **4** was rather interesting because oxidation selectively stops at the stage of *p*-tolylic acid (**10**) without any formation of terephthalic acid, even when more than two equivalent ozone were added. This is a main advantage of this method in comparison to classical benzylic oxidation methods where oxidation can hardly be stopped on the stage of the monooxidation product **10** [1]. The observed selectivity can easily be explained by comparing the Hammett coefficients of the methyl group ($\sigma = -0.17$) and the carboxylic group ($\sigma = 0.45$). While the aromatic system, and therefore also benzylic position, is highly activated by the methyl substituent, the reaction proceeds rapidly as long as any xylene is remaining. As soon as **4** is oxidised to the mono-acid **10**, the second methyl group is deactivated by the formed carboxylic acid and thus, further oxidation is inhibited. Oxidation of **4** in Ac₂O also proceeded with total conversion giving over 70% of *p*-tolualdehyde (**11**) and over 20% of 4-methyl-benzylacetate (**12**).

Selective oxidation of compounds with neutral substituents, such as toluene, has recently been reported [11,12]. Oxidation of slightly deactivated compounds, such as **5** was
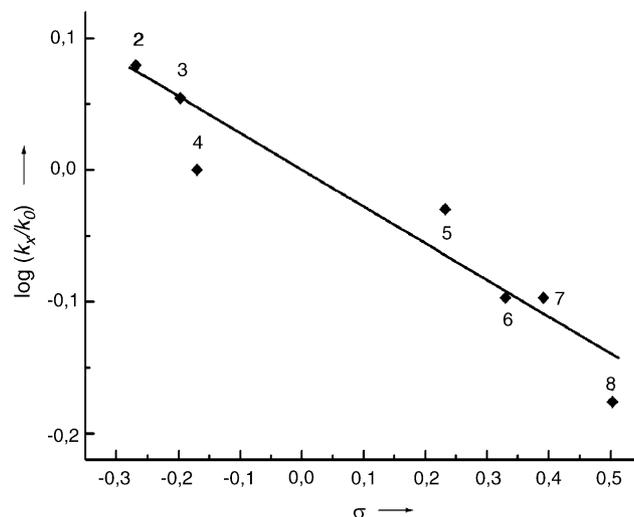

Fig. 1. Hammett plot for the transition metal catalysed oxidation of various substituted toluene derivatives by ozone.

also possible with total conversion and in high selectivity, but it was also found, that these compounds cannot be oxidised with milder catalyst systems like those used in the oxidation of **2** any longer. With increasing Hammett coefficient of the substituent, a decreasing reactivity of the compound could be observed. This was clearly shown in the oxidation of **6**, which proceeded selectively, but with a rather low conversion rate. The conversion rate in this reaction could be improved by using a higher concentrated catalyst system and addition of three equivalents ozone, but conversion still was limited to 36%. Accordingly, the methyl group of this compound seems to be too inactive for a complete oxidative conversion. Substrate **8** followed the observed trend, which means that the reactivity of this compound is less than that of **6** (due to the increased electron pressure as indicated by an increased Hammett coefficient). Whereas, in AcOH at least 8% conversion was observed, an oxidation in Ac₂O was impossible. Finally, oxidation of the highly deactivated **9** showed a very low ozone uptake of the reaction solution and no conversion under standard conditions. The only observed exception (regarding their Hammett coefficients) in this screening series was oxidation of **7**, which by means of a slightly stronger catalyst system proceeded similarly selective and also with the same high conversion rate as that of the more activated 4-bromo derivative **5**.

Although the observed ozone uptake of the reaction solution under standard conditions clearly indicates the reactivity of a compound, it was interesting to quantitate the relationship between reactivity (reaction rates) of these compounds and the Hammett coefficients of the substituents. Thus, the rates obtained for the oxidation of the substituted derivatives were compared with the rate of the oxidation of toluene. Fig. 1 shows the resulting Hammett plot, which displays a good correlation of the σ parameters and the ozonisation rates resulting in a reaction constant $\rho = -0.279$. From the negative sign of the latter it immediately follows that the re-

action is activated by high electron density at the reaction centre.

It has to be mentioned that the result for the oxidation of the most activated compound **1** could not be included due to the limited ozone feed under the chosen conditions. The rate for the most deactivated substrate **9** could also not be determined with sufficient precision due to the exceedingly small ozone uptake.

3.2. Steric influences

To investigate the influence of steric effects on conversion and selectivity of this Mn(II) catalysed ozonisation reaction, 2- and 4-bromotoluene (**13** and **5**) were oxidised. As the Hammett coefficients for *ortho* and *para* substituents can be considered the same [1], different reactivities of these two compounds can only be explained to result from steric influences of the bromine substituent on the benzylic group. Indeed we observed a lower conversion rate (<75%) and also a significantly lower selectivity in the oxidation of 2-bromotoluene (**13**) than for the 4-isomer **5**, which suggests the steric influence of substituents on the reaction center. 2-Bromobenzoic acid (**14**) was obtained with 70% and 2,4-dibromotoluene (**15**) with about 20% selectivity. As a possible explanation for the formation of **15** a disproportionation reaction [21] of **13** yielding **15** and toluene might be assumed.
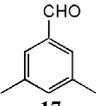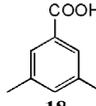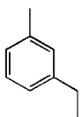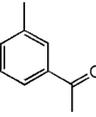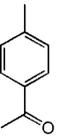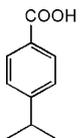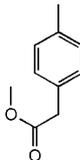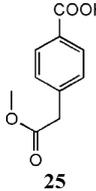
### 3.3. Compounds with additional benzylic positions

We have already mentioned the use of the Mn(II) catalysed ozonisation method for the selective oxidation of compounds with additional benzylic positions (e.g. tetraline) [11,12]. We now investigated the transition metal catalysed oxidation of several compounds with additional primary, secondary, and tertiary benzylic positions. The question was, which groups would be more reactive and whether a similarly selective monooxidation as in the case of **4** is possible.

Thus, it was demonstrated, that selective monooxidation of mesitylene (**16**) is also possible using this method. Although reaction conditions were not optimised, a rather high conversion rate and selectivity were observed. Surprisingly, the corresponding aldehyde **17** turned out to be the main product after the addition of 2 equivalents ozone in AcOH, but an eventual oxidation of the reaction solution with H_2O_2 led to a total conversion of **17** to the corresponding acid **18**, which could be obtained with an overall yield of nearly 65%.

In all cases oxidation of the different benzylic groups of **19**, **22**, and **24** proceeded simultaneously to yield **20** + **21**, **8** + **23**, and **10** + **25** + **26** + **27**, but a multiple oxidation was never observed. This can be explained similarly as for the oxidation of **4**. As soon as one benzylic group is oxidised this leads to a deactivation of the second one as a result of

Table 2
Oxidation of toluene derivatives with additional benzylic groups by O_3/Mn(II) in AcOH

Compound	Conversion rate (%)	Product yields		Comment
Mesitylene (**16**)	90	**17** 40%	**18** 25%	Afterward oxidation of **17** to **18** with H_2O_2
m-Ethyltoluene (**19**)	100	**20** ≥ 70%	**21** ≤ 25%	Monooxidation
p-Cymene (**22**)	85	**8** ≥ 65%	**23** ≤ 30%	Monooxidation
Methyl-4-tolylacetate (**24**)	≤25	**10** + **26** + **27** ≤ 45%	**25** ≥ 50%	Monooxidation
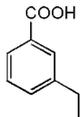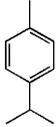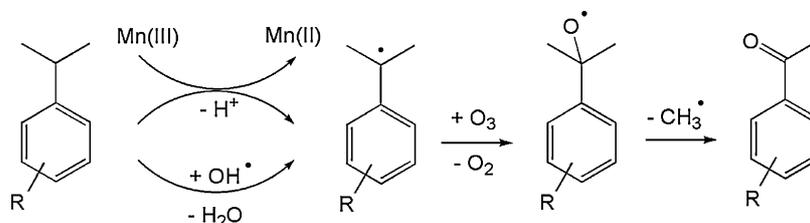
Scheme 2. Suggested mechanism for the conversion of the *i*-propyl group to the acetyl group via a mechanism including radical species.

the introduction of an electron withdrawing carbonyl group bonded to the aromatic ring. Oxidation of the higher activated group proceeded faster and therefore in higher selectivity, but oxidation of this group never proceeded quantitatively. Therefore, in all cases a product mixture of at least two different oxidation products was obtained. It has to be mentioned, that in no case efforts of optimizing the reaction were made. For compounds with different benzylic groups, electronic properties of these groups determine which one is more reactive towards an oxidative attack. In the case of **19**, the predominating oxidation of the ethyl group to give a higher yield of **20** than of **21** can be explained by the higher electron density at the secondary benzylic group in comparison to the primary benzylic group. Quite similar results were obtained in the oxidation of **22**, where oxidation of the higher activated *i*-propyl group was preferred to yield more of **8** than of **23**. Substrate **24** turned out to be rather deactivated towards an oxidative attack and was the only derivative where the primary benzylic group was more reactive than the secondary. This can be rationalised by the deactivation of the methyl group by the electron withdrawing acetate group on the one hand, and by the deactivation of the methylene group by the formate group on the other hand. Oxidation of the methylene group of **24** gave several oxidation products, like methyl-(4-methyl)benzoylformate (**26**) and the cleavage products **10** and 4-methyl-benzyl alcohol (**27**). Comparing the results obtained for the oxidation of **19** and **24**, it is evident that the methylene group of ethyl substituents is activated by the slightly electron donating methyl group, whereas the methylene group of acetate substituents is deactivated by the electron withdrawing formate group. In the cases of **19** and **22**, variation of the catalyst concentration can slightly influence the oxidation ratio between primary and secondary/tertiary benzylic groups, but still with a predominating oxidation of the higher activated secondary/tertiary groups. We found that less sulfuric acid and more Mn(II) acetate improved the oxidation of the methyl group.

3.4. Mechanistic considerations

To obtain information about the reaction mechanism of transition metal catalysed ozonisations, oxidation of *p*-cymene (**22**) was considered. On the one hand, Tyupalo and Yakobi [22] proposed that metal-catalysed ozonisation is initiated by the formation of a high-valent metal ion species giving Mn(III) and free •OH radicals. On the other hand, Ja-

cobson et al. [23] suggested an oxygen atom transfer to give the "manganyl" ion MnO^{2+}, avoiding the formation of •OH radicals. With respect to the oxidation of **22** this means: if a metal-oxo transfer mechanism is favoured, oxidation of the methyl group giving **23** as the main product should predominate, whereas oxidation of the *i*-propyl group to yield **8** would indicate a mechanism including radical species. Now, oxidation of the *i*-propyl group turned out to be predominant with over 65% selectivity under standard conditions (see Table 2), which favours a mechanism including radical species. According to Tyupalo and Yakobi [22] and Partenheimer [1] a plausible reaction mechanism for this reaction can be suggested involving an initial radical abstraction of hydrogen, followed by the formation of an *i*-propyloxyl radical. The final step is the abstraction of a CH_3 radical forming the acetyl group, as shown in Scheme 2.

4. Conclusion

It was shown, that transition metal catalysed oxidation by means of ozone is a quite useful and selective method for the oxidation of benzylic compounds. It was found, that conversion and selectivity in this type of reaction widely changes with the nature of the substituent. Electron donating substituents enhance the reactivity towards an oxidative attack, whereas selective oxidation of compounds with electron withdrawing substituents is rather difficult or even impossible. According to the obtained results, the reactivity of a benzylic compound can be described by the Hammett coefficient of its substituent. But also the stability of the chosen substituent under given reaction conditions has to be regarded. In addition, it was found that steric effects have an influence on the reactivity of the benzylic position. So, if the Hammett coefficient and the stability of a substituent under certain conditions are known, predictions about the selective oxidation of a compound with this method can be advanced.

Upon oxidation of compounds with different benzylic groups the electronic properties of these groups determine which one is more reactive. It was found, that secondary and tertiary benzylic groups are more reactive than primary ones. We also demonstrated the high selectivity in oxidising compounds with more than one benzylic group. Thus, selective monooxidation of such compounds is possible quite easily using this method. Another aim of the experiments carried out was the investigation of the reaction pathway. Accord-

ing to the results obtained in ozonisation of *p*-cymene, the transition metal catalysed oxidation of benzylic groups by means of ozone proceeds via one-electron transfer radical reactions.

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