

Montmorillonite Substrate Selectivity in Alcohol Oxidation

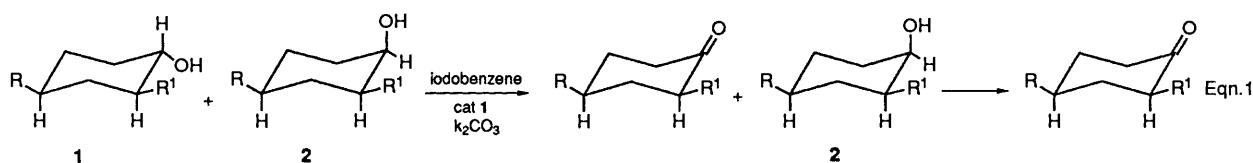
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An unusual display of sequential and preferential molecular recognition in favour of *trans-tert*-butylcyclohexanols **1**, primary alcohols **3** and *o*-benzyl alcohols as against *cis-tert*-butylcyclohexanols **2**, secondary alcohols **4** and *p*-benzylalcohols, respectively, is described.

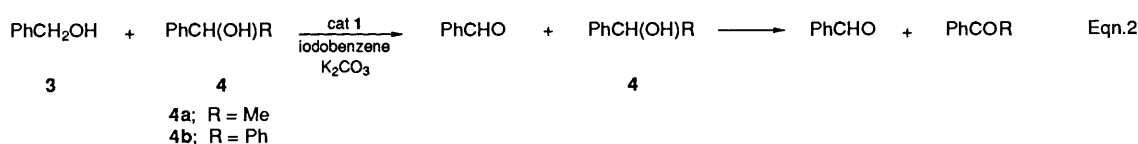
Substrate selectivity imparted by non-enzymatic materials is of topical interest.¹⁻⁸ A recent report, from our laboratory, of the sequential and preferential selectivities of *ortho* isomers over *para* isomers of iodobenzenes in the arylation of acrylates using montmorillonite-anchored catalyst, forms one of the most important discoveries in this area.⁹ We thus successfully demonstrated the sequential formation of products using mixtures in the place of pure compounds in the reaction, for the first time. Laszlo and co-workers observed similar novel and

remarkable effects in the alkylation of aromatic hydrocarbons in the presence of montmorillonite K₁₀ impregnated with zinc chloride¹⁰ or ferric chloride.¹¹ We report here an unusual display of sequential and preferential selectivities in specially chosen sets of alcohol pairs, such as stereoisomers, eqn. (1), primary and secondary benzyl alcohols, eqn. (2), and *ortho* and *para* isomers of benzyl alcohols (Table 1) in a competitive oxidation reaction using as catalyst montmorillonite-silylethyl-diphenylphosphinepalladium(II) chloride (cat **1**).¹²



1a = 2a R = H, R¹ = *tert*-butyl

1b = 2b R = *tert*-butyl, R¹ = H



4a; R = Me
4b; R = Ph

Table 1 Substrate selectivity of alcohols in oxidation

Entry No.	Substrate S ₁	Substrate S ₂	Relative rates of S ₁ /S ₂ in individual reactions	Ratio of S ₁ :S ₂ in competitive reaction ^a
1	PhCH ₂ OH	PhCH(OH)Me	5.0/4.5	100:20 (78:100)
2	PhCH ₂ OH	Ph ₂ CHOH	5.0/4.0	100:1 (76:100)
3	PhCH(OH)Me	Ph ₂ CHOH	4.5/4.0	100:<5 (100:90)
4	PhCH(OH)Me	MeOC ₆ H ₄ CH(OH)Me- <i>p</i>	4.5/4.0	100:34 (100:85)
5	PhCH(OH)Me	PhCH(OH)CH ₂ C ₆ H ₄ OMe- <i>p</i>	4.5/4.5	100:10 (100:87)
6	HOCH ₂ C ₆ H ₄ OMe- <i>o</i>	MeOC ₆ H ₄ CH ₂ OH- <i>p</i>	4.5/4.0	100:1 (90:100)
7	HOCH ₂ C ₆ H ₄ OMe- <i>o</i>	MeC ₆ H ₄ CH ₂ OH- <i>p</i>	4.0/4.4	100:48 (92:100)
8			R = Bu ^t 6.0/8.0 R = Me 6.0/5.5	100:<1 (100:95) 100:95 (100:92)
9			R = Bu ^t 5.0/8.0 R = Me 6.0/5.8	100:1 (100:90) 100:97 (100:95)

^a The values in parenthesis are with an analogous Pd-phosphine complex in homogeneous environment. The yields in the individual and competitive reactions are near quantitative for all the set of reactions as indicated by GC-NMR. The isolated yield for the reaction in entry 1 is 93% (PhCHO) and 95% (PhCOMe).

Typical Procedure for the Oxidation of Alcohols.—Competitive reactions.* A mixture of cat **1** (0.05 mmol of palladium; 300 mg), potassium carbonate (12 mmol), iodobenzene (12 mmol) and DMF (20 cm³) under an inert atmosphere was heated at 80 °C for 0.5 h. A mixture of substrates S₁ and S₂ (5 mmol each) was then introduced and the temperature was raised and maintained at 110 °C until the reaction was complete. The reaction sequence was followed by GC-NMR.

Individual reactions. The procedure described above was followed except that in place of a mixture of substrates each individual substrate was allowed to react. Relative rates indicated in Table 1 denote the time taken for completion of the reaction.

Impressive sequential and preferential substrate selectives towards (a) primary benzyl alcohols in the presence of secondary benzyl alcohols (entries 1 and 2), (b) 1-phenylethanol (entry 3) in the presence of diphenylmethanol (entry 3) and phenyl(benzyl)methanol (entry 5) are displayed in competitive oxidations, although the relative rates of the individual reactions are nearly the same.† In contrast, no significant preferential selectivity towards either of the substrates is displayed in the analogous palladium-phosphine complex in an homogeneous environment. Therefore the substrate selectivity displayed by catalyst **1** is attributed to the effect of montmorillonite. The striking substrate selectivity of a primary benzyl alcohol in the presence of a secondary benzyl alcohol is an unusual example of catalytic oxidation.

The situation with respect to isomers of cyclohexanols is very interesting since, remarkably, total sequential and preferential substrate selectivity is observed towards the *trans*-isomers in the presence of *cis*-isomers of *tert*-butyl cyclohexanols (entries 8 and 9). In contrast, the catalyst failed to achieve any substrate selectivity in competitive oxidations conducted with sets of analogous isomers of methylcyclohexanols. This suggests that replacement of a methyl group with a *tert*-butyl group could afford quantitative discrimination of *cis*-alcohols. The result of

near quantitative to moderate discrimination of the *para* isomer in favour of the *ortho* isomer of benzyl alcohols (entries 6 and 7) is consistent with the substrate selectivities found in arylations.⁹

The substrate selectivities achieved reflect an interplay between the substituents on the substrates *vis-à-vis* oxygens and hydroxy groups of the support and the result of non-preferential substrate selectivities the parallel experiments conducted with analogous palladium-phosphine complex in a homogeneous environment further strengthens this argument. The successful substrate selectivities have great potential in synthetic organic chemistry, since the inseparable reaction mixtures may be used directly without the use of cumbersome separation techniques.

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* Oxidations catalysed by a palladium complex, using iodobenzene as an oxidant in presence of base is a model reaction.^{1,3}

† A similar observation was made in the arylation of acrylates (ref. 9) and alkylations (ref. 10 and 11) using a montmorillonite support.

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