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PHOTO-OXIDATION OF ALCOHOLS CATALYSED BY PLATINISED TITANIUM DIOXIDE

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Summary: Irradiation of alcohols in benzene in the presence of platinised titanium dioxide provides a clean and convenient procedure for the synthesis of aldehydes and ketones on preparative scale.

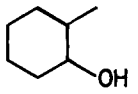
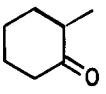
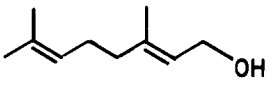
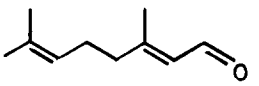
Titanium dioxide powders are known to catalyse a whole variety of organic photochemical oxidations and fragmentation reactions.[1] We now report that platinum supported on titanium dioxide acts as an excellent sensitizer for the oxidation of alcohols to aldehydes and ketones on preparative scale.[2]

A vigorously stirred suspension of platinised titanium dioxide (25mg.,0.5%Pt)[3] in dry benzene (10ml) containing the alcohol (0.1g) was purged with nitrogen, and then irradiated using a 400W high pressure mercury lamp (8-15h). The catalyst was removed by filtration through diatomite and the products were then purified by chromatography on silica using ether-light petroleum (b.p. 40-60°C) (1:25-1:12) as eluant. The results are summarised in the Table.[4]

Both the aromatic secondary alcohols and the aliphatic primary alcohols studied yielded the corresponding ketones and aldehydes respectively, in excellent yields (60-98%). These yields were not improved when acetonitrile was used as solvent in place of benzene, or when a catalyst bearing a higher proportion of platinum (up to 1.7%) was employed. In no case did we observe further oxidation of the aldehyde products to the corresponding carboxylic acids.

By contrast, the oxidations of aliphatic secondary alcohols and 2-methylcyclohexanol gave poor yields of carbonyl products (<30%). The recovery of substantial amounts of starting alcohols from the reactions suggested that these poor yields were not associated with competing side reactions. Indeed a competition experiment, using a mixture of octan-1-ol and 6-methylhept-5-en-2-ol led to only 15% 6-methylhept-5-en-2-one when all the octanol had been converted into octanal. This observation suggests that the present method could have practical advantages as a mild and convenient procedure for the selective oxidation of primary alcohols in the presence of secondary aliphatic alcohols.

TABLE. Photo-oxidation of Alcohols to Aldehydes and Ketones using Platinised Titanium Dioxide

Alcohol	Product	Yield(%)[a]
Ph_2CHOH	Ph_2CO	98
PhCH(OH)Me	PhCOMe	83
$\underline{n}$-$C_7H_{15}CH_2OH$	$\underline{n}$-$C_7H_{15}CHO$	70
$Me_2C{:}CH\ CH_2\ CH_2\ CH(OH)Me$	$Me_2C{:}CH\ CH_2\ CH_2\ COMe$	29[b]
		11[b]
		75[c,d]

[a]based on isolated products after chromatography; [b]starting material (65-70%) recovered by chromatography; [c]a 1:1 Z-E mixture was produced; [d]a small amount (<10%) of (±)-citronellal was produced concurrently.

The oxidation of geraniol in the presence of platinised titanium dioxide was interesting, leading to a 1:1 mixture of Z - and E-citral accompanied by a small amount (<10%) of (±)-citronellal. The citronellal produced in this reaction is clearly the result of in situ 'back hydrogenation' of the citral product.

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References

1. For a review and some recent work see: M. A. Fox, Acc. Chem. Res., 1983, 16, 314; C. Giannotti, S. Le Greneur and O. Watts, Tetrahedron Lett.,1983, 24, 5071; R. S. Davidson and J. E. Pratt, ibid, 1983, 24, 5903.

2. For kinetic studies of the oxidation of aliphatic alcohols catalysed by TiO_2 and Pt/TiO_2 see: P. R. Harvey, R. Rudham and S. Ward, J. Chem. Soc., Faraday Trans. I, 1983, 79, 2975; P. Pichat, M-N. Mozzanega, J. Disdier and J-M. Herrmann, Nouv. J. Chim., 1982, 6, 559, and references therein.

3. $Pt(0.5\%)/TiO_2$ was prepared by photodeposition on Degussa P25 anatase: E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca and M. Grätzel, J. Am. Chem. Soc., 1981, 103, 6324.

4. Yields are based on isolated pure compounds, whose spectral data were identical with those of authentic samples.

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