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LETTERS

A Novel Oxidative Cleavage Reaction of Propargyl Alcohol Derivatives using K_2FeO_4-Al_2O_3

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Abstract: Recent work has shown that a new K_2FeO_4 based oxidation protocol can promote a highly unusual carbon-carbon bond cleaving reaction of functionalised propargyl alcohols.

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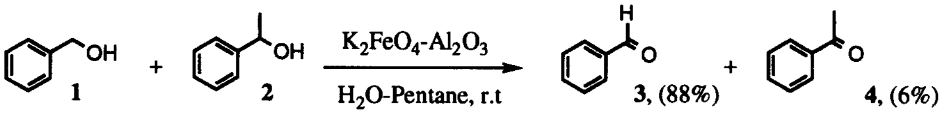
The oxidation of organic compounds is one of the most fundamental organic transformations and there has been enormous activity in the development of new reagents [1]. There has been sporadic interest in the use of the ferrate (VI) ion for the oxidation of organic substrates and potassium ferrate is attractive because of its potential to deliver an environmentally acceptable, non-toxic alternative to more conventional reagent systems. There have been reports on the oxidation of alcohols using potassium ferrate under a range of conditions [2] [3].

Our preliminary oxidation studies demonstrated that activated primary aromatic alcohols could undergo oxidation using a K_2FeO_4-Al_2O_3 reagent system. These reactions were carried out in the presence of wet alumina (20-40%) in pentane as solvent. Secondary alcohols were much less reactive toward this system and there appears to be some inherent selectivity as is highlighted in the oxidation of a (1:1) mixture of benzaldehyde **1** and *sec*-phenethyl alcohol **2** as shown in scheme 1 (isolated yields of 3 (88%) and 4 (6%)). This reactivity pattern highlights the mildness of the procedure compared with other ferrate oxidation protocols.



Scheme 1

However of particular note was the behaviour of activated propargylic alcohol derivatives with the new reagent system which are presented in table 1. Thus treatment of mono-protected diol **5** with wet K_2FeO_4-Al_2O_3 in pentane at room temperature gave the terminal alkyne **6**. This remarkable C-C bond cleaving process was also observed with substrates **7**, **9** and **11** which incorporate an alkyl spacer group between the protected oxygen functionality and the reactive centres. The lack of success with an alkyl substituted alkyne **13** and the silicon protected substrate **15** suggests the involvement of a co-ordinating oxygen functionality. The ability of potassium ferrate to promote such carbon-carbon bond cleaving reactions is without precedent. Indeed the only

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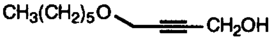
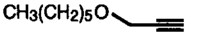
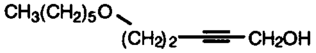
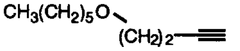
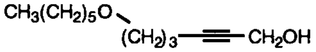
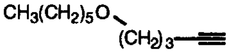
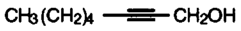
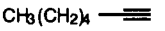
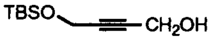
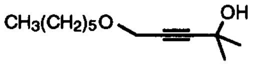
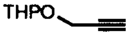
related reaction we have been able to identify from the literature is the base-mediated cleavage of tertiary propargylic alcohols [4]. When we subjected tertiary alcohol **17** to the oxidation conditions we observed no reaction. Thus it would appear that the present cleaving reaction is mechanistically, as well as operationally different from the known base-mediated reaction.

Table 1: Oxidative Cleavage of Primary Activated Propargyl Alcohols using K_2FeO_4-Al_2O_3

Entry	Substrate		Product		t (h)	Yield (%)
1		5		6	2	52
2		7		8	24	96
3		9		10	120	23-25
4		11		12	120	33
5		13		14	48	0
6		15		16	48	0
7		17		18	48	0

All reactions carried out using K_2FeO_4-Al_2O_3 (1 eq) in pentane at room temperature.

In summary we have observed a new oxidative transformation promoted by K_2FeO_4-Al_2O_3. The reaction, which as far as we can determine is unprecedented for any ferrate oxidant, is intriguing and appears to be dependant upon participation from a neighbouring (co-ordinating) oxygen. This remarkable effect appears to facilitate the C-C bond cleaving reaction of propargyl alcohol derivatives. These observations may suggest ways for unleashing the considerable potential that potassium ferrate has for new oxidative transformations of organic substrates.

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