Tetrahedron Letters,Vol.31,No.3,pp 353-356,1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

ON THE OXIDATION OF 3-ETHYLPENTANE UNDER GIF^{IV} AND GIF-ORSAY CONDITIONS

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Abstract - The oxidation of 3-ethylpentane under Gif^{IV} (and GoAgg^{II}) conditions affords, as major product, 3-acetylpentane and not diethylketone as previously reported. The discrepancy is explained by radical chain autoxidation in presence of a weak tertiary C-H bond.

The selective activation of saturated hydrocarbons is a topic of current interest.[1] One approach involves porphyrin models of P450 enzymes.[2] There is considerable agreement that in these systems an iron-oxo species is present which behaves like an alkoxyl radical.[3] As a result the selectivity order is tert.> sec.> prim.

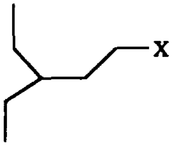
We have adopted a different approach using Gif type systems. These have the interesting property of oxidising saturated hydrocarbons to ketones, with minor attack at primary and tertiary positions (selectivity: sec.> tert.≥ prim.). Saturated hydrocarbons are oxidised faster than primary or secondary alcohols or ethers. Radical chemistry is a minor component of the observed reactivity.[4,5]

Amongst the Gif type systems we mention Gif^{IV} (pyridine-acetic acid as solvent, Fe^{II} catalyst, O_2 and zinc dust as a source of electrons), Gif-Orsay (the same as Gif^{IV}, but with the zinc dust replaced by the cathode of an electrochemical cell) and GoAgg^{II} (pyridine-acetic acid as solvent, Fe^{III} catalyst and hydrogen peroxide).[6] All these systems involve the same Fe^{V} oxenoid species which inserts itself into the C-H bond to give an iron-carbon bond which evolves, at a secondary position, into ketone[6] and may, at the tertiary position, give radicals.

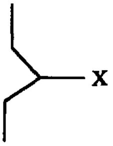
The following saturated hydrocarbons have been oxidised in accordance with our general observations : adamantane,[4,5] methylcyclohexane,[4] methylcyclopentane,[4,5] isopentane,[4] *cis*-decalin,[4,5] *trans*-decalin.[4,5] We were surprised therefore when 3-ethylpentane **1** gave diethylketone[5] as the major product of the reaction under

Gif ^{IV} and Gif-Orsay conditions. This could have come from the tertiary alcohol **2**, but a blank experiment gave little oxidation to diethylketone. Since these observations were a major anomaly, we have investigated the matter further.

3-Ethylpentane **1** was conveniently prepared from the alcohol **2**[5] by tosylation and reduction with lithium aluminum hydride. It was identical with a specimen prepared as before[5] from triethylcarbinol. The latter also afforded **1** in one step using triethylsilane reduction of the carbonium ion.[7] 3-Ethylpentan-2-one **3** was conveniently prepared from cyanide displacement on pentan-3-ol mesylate to give **4**. Addition of methyl lithium and hydrolytic work up gave **3**. Other authentic specimens were prepared as before.[5]

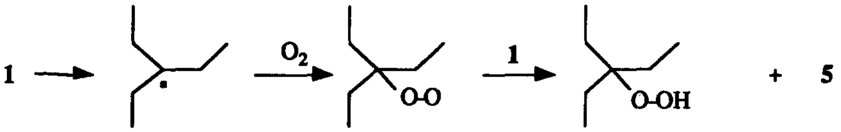


1 X = H
2 X = OH



3 X= COMe
4 X = CN

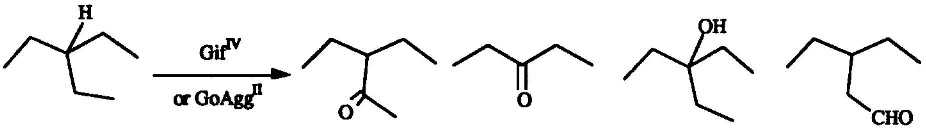
The oxidation (Table 1) of 3-ethylpentane **1** under Gif^{IV} and GoAgg^{II} conditions (see footnotes to the Table) gave as the major product the ketone **3**. Only traces of diethylketone were formed. The previous experiments[5] were carried out chemically with Gif^{IV} and electrochemically (Gif-Orsay), the latter with a vigorous stream of oxygen. We can conclude that we inadvertently started a conventional radical chain reaction involving (Scheme) the conversion of the weak tertiary hydrogen to the 3-ethylpentyl radical **5**. The latter would furnish the peroxide radical **6** which would continue the chain to give the hydroperoxide **7**. Conventional ferrous ion cleavage would then give the previously observed product, diethylketone.



5 **6** **7**

Scheme

Table 1. Oxidation of 3-Ethylpentane 1 uner Gif^{IV} and GoAgg^{II} condition



1 3 8 9 10

Reaction Type	^{c} Products 3	8	9	10	1 recovered %	Mass Balance %
^{a}Gif^{IV}	7.7	<1	1.2	3.0	85	97
^{b}GoAgg^{II}	7.0	<1	1.8	1.4	79	89

^{a} A solution of 1 (250 mg, 2.5 mmol) in pyridine (14 ml) - AcOH (1.15 ml, 20 mmol) containing $FeCl_2 \cdot 5H_2O$ (10 mg, 0.05 mmol) and zinc powder (900 mg, 14 mmol) was stirred under a balloon of O_2 for 16 hrs. at room temperature. ^{b} To a pyridine (14 ml), AcOH (1.15 ml, 20 mmol) solution of 1 (250 mg, 2.5 mmol) and $FeCl_3 \cdot 6H_2O$ (27 mg, 0.10 mmol) a 30% aqueous solution of H_2O_2 (1 ml, 9 mmol) was added in one portion and stirred in a closed flask at room temperature. ^{c} Both reaction mixtures were extracted with ether after acidification (dilute H_2SO_4) and analysed by GC and GC-MS.

We confirmed that triethylcarbinol gives small amounts of diethylketone under Gif^{IV} conditions as does the ketone 3. However, the rates of these reactions could not explain the previously observed[5] quantities of diethylketone.

Thus, there is no exception to Gif type selectivity. The origin of the radical 5 may well be the fission of a tertiary iron-carbon bond to give a carbon radical.[4] Such problems can, of course, be avoided with GoAgg^{II}.

Acknowledgements. We thank the N.S.F. for the partial support of this work. One of us (D.D.) is recipient of a Merck Sharp and Dohme Post-doctoral Fellowship.

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(Received in France 20 October 1989)