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GIF-TYPE OXIDATION SYSTEMS. EVIDENCE FOR A SECOND INTERMEDIATE BETWEEN SATURATED HYDROCARBON AND KETONE

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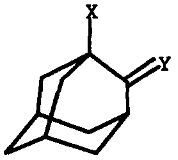
Abstract: The addition of dianisyl telluride to a Gif^{IV} oxidation of adamantane has a marked effect on the ratio of ketone to secondary alcohol formed. This is interpreted as an indication of a second intermediate in the conversion of saturated hydrocarbons into ketones. This second intermediate is probably an Fe^{III} alkoxide.

Gif-type oxidation systems convert saturated hydrocarbons selectively to ketones in a reaction which is without precedent.[1] There is good evidence for an intermediate **A** in this conversion.[2] **A** can be efficiently captured by PhSeSePh, PhSSPh, $CHBr_3$ and CCl_4. Recent work has shown that $BrCCl_3$ is an even better brominating agent than $CHBr_3$.[3] This kind of reactivity would be characteristic of carbon radicals were it not that studies with pyridine at controlled oxidation pressure show that radicals are not trapped as they should be from studies under comparable conditions with genuine secondary radicals.[4,5] Also hydrogen sulfide, a good trap for radicals, does not interfere in the ketonization process.[6,7]

The purpose of this communication is to report that there is also a second intermediate **B**, which affords *sec.*-alcohol on hydrolysis and gives ketone under normal oxidation conditions. It has already been carefully established that under Gif^{IV} type oxidation conditions, *sec.*-alcohol is not converted into ketone and ketone is not converted into *sec.*-alcohol.[8]

Adamantane **1** (2 mmol) in pyridine (28 ml) containing $FeCl_2.4H_2O$ (0.05 mmol) and zinc powder (1.30 g ;20 mat.) was stirred under air and acetic acid (2.3 ml; 40 mmol) was added. These are typical Gif^{IV} conditions and give the usual results shown in Table 1.

When dianisyl telluride (An_2Te) was added to Gif^{IV} oxidation in increasing amounts (Table 1), there was a marked effect on the ratio of *sec.*-alcohol to ketone. As the amount of An_2Te was increased from 0.5 mmol to 2 mmol, which is a large excess with respect to the amount of hydrocarbon oxidized, the *sec.*-alcohol increased from 3% (no An_2Te) to



1 X = H, Y = H_2

2 X = OH, Y = H_2

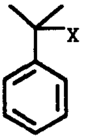
3 X = H, Y = O

4 X = H, Y = H, OH

5 X = 2′-Py, Y = H_2

6 X = H, Y = H, 2′-Py

7 X = 4′-Py, Y = H_2



8 X = O-OH

9 X = OH

Table 1

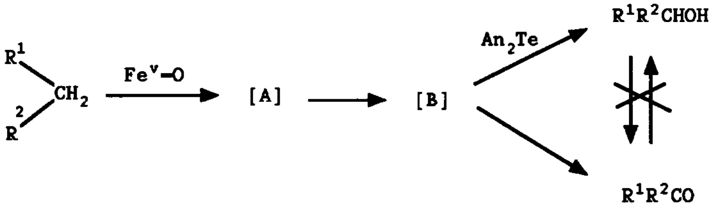
Products, etc.	Gif^{IV}	Gif^{IV} +0.5 mmol An_2Te	Gif^{IV} +1.0 mmol An_2Te	Gif^{IV} +2.0 mmol An_2Te
2	1.1	2.7	2.2	1.4
3	16.1	7.7	4.7	3.6
4	2.9	9.7	9.1	6.6
5	5.0	5.4	2.9	4.4
6	<0.1	0	0	0
7	12.6	12.2	6.8	8.5
C^2/C^3 [a]	17.2	6.4	6.3	7.3
C^2/C^3 [b]	1.02	0.86	1.16	0.71
1 (recovered)	61.3	57.8	67.0	67.2
Mass Balance	99	99	93	94

[a] Without pyridine coupled products

[b] With pyridine coupled products

nearly 10% while the ketone fell from 16% to 8% or less. For 0.5 mmol An_2Te the total of ketone plus secondary alcohol decreased only from 19.0 to 17.4%, although the oxidation products and An_2Te are in comparable amounts. In contrast, the ratio of ketone to secondary alcohol changed from 5.5 to 0.8. It was noteworthy that no *sec.*-pyridyl derivatives were formed, in agreement with previous observations.[4,8]

In order to understand why An_2Te has a minor effect on total oxidation, but a major effect on the ketone-secondary alcohol ration, we examined the reactivity of this reagent on a typical hydroperoxide **8** (Table 2). In each case **8** was reduced nearly quantitatively to **9**, in agreement with a two electron reduction process.



Scheme 1

Table 2

8 mmol	An_2Te mmol	**9** (%)	An_2TeO (%)	Conditions
0.5	0.5	99	98	Pyridine, R.T. 10 min. air
2.0	4	100	37[a,b]	Pyridine-AcOH (10:1) 10 min. R.T. air
1.0	1	100	70[b]	Same conditions
0.5	0.5	94	51[b]	Under N_2

[a] An_2Te (48%) was also recovered.
[b] Isolated as $An_2Te(OAc)_2$.

The simplest interpretation of these results is that the intermediate **A** is converted to ketone in two steps (Scheme 1). The first step is the formation of a second intermediate **B** in which oxidation has taken place to the secondary alcohol level. Normally **B** is oxidized further to ketone, but in the presence of An_2Te this process is much less efficient. The secondary alcohol is released without further transformation. The most probable formulation of **B** is as an alkoxide of ^{III}Fe. The oxidation process that is interrupted by the An_2Te could well be a reduction of an oxygen-oxygen bond (see above), but reduction of an iron oxo-species is also possible.

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