

FUNCTIONALISATION OF SATURATED HYDROCARBONS. Part X.<sup>1</sup>  
A COMPARATIVE STUDY OF CHEMICAL AND ELECTROCHEMICAL PROCESSES  
(GIF AND GIF-ORSAY SYSTEMS) IN PYRIDINE, IN ACETONE  
AND IN PYRIDINE-CO-SOLVENT MIXTURES\*

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*Abstract - Six saturated hydrocarbons (cyclohexane, 3-ethylpentane, methylcyclopentane, cis- and trans-decalin and adamantane) were oxidised by the Gif<sup>IV</sup> system (iron catalyst, oxygen, zinc, carboxylic acid) and its electrochemical equivalent (Gif-Orsay system). Results obtained using various solvents (pyridine, acetone, pyridine-acetone mixtures) were similar for both systems. Total or partial replacement of pyridine with acetone affects the selectivity for secondary positions and lowers the ketone/secondary alcohol ratio. The formation of the same ratio of cis- and trans-decal-9-ol from both cis- and trans-decalin clearly demonstrates that tertiary alcohols result from a mechanism essentially radical in nature.*

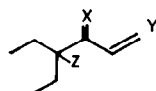
In previous articles<sup>2,3</sup> we highlighted the specificity of what we call the Gif system for oxidation of saturated hydrocarbons, i.e. high yield of oxygenated products when compared to analogous systems and selective mono-oxygenation, ketones being always the major products. More recently, we reported an electrochemical modification<sup>4,5</sup> in which a mercury cathode replaces the zinc powder used as reductant in the catalytic Gif<sup>IV</sup> system [catalytic amounts of iron cluster Fe<sub>3</sub>O(OAc)<sub>6</sub>Pyr<sub>3,5</sub>, zinc powder, pyridine, acetic acid, molecular oxygen at 20-30°C]. At present, the Gif-Orsay electrochemical system comprises catalytic amounts of iron cluster Fe<sub>3</sub>O(OAc)<sub>6</sub>Pyr<sub>3,5</sub>, a trifluoroacetic acid/pyridine mixture as source of protons and electrolyte; a mercury pool as cathode, a platinum anode and molecular oxygen as the ultimate oxidant. This system in which a one-compartment electrochemical cell is used, is able to oxidise saturated hydrocarbons with the same specificity as the chemical system, but with

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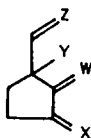
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Texas 77843, U.S.A.  
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91128 Palaiseau, France.



- 1 X = H<sub>2</sub>  
2 X = O  
3 X = H, OH  
4 X = H, 2' or 4' pyridyl

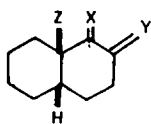


- 5 X = Y = H<sub>2</sub>; Z = H  
6 X = O, Y = H<sub>2</sub>; Z = H  
7 X = H, OH; Y = H<sub>2</sub>; Z = H  
8 X = Y = H<sub>2</sub>; Z = OH  
9 Y = O; X = H<sub>2</sub>; Z = H  
10 Y = H, OH, X = H<sub>2</sub>; Z = H

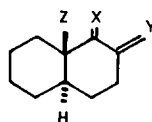


- 11 W = X = Z = H<sub>2</sub>, Y = H  
12 W = O; X = Z = H<sub>2</sub>, Y = H  
13 X = O; W = Z = H<sub>2</sub>, Y = H  
14 W = H, OH; X = Z = H<sub>2</sub>, Y = H  
15 X = H, OH; W = Z = H<sub>2</sub>, Y = H  
16 W = X = Z = H<sub>2</sub>, Y = OH  
17 W = X = H<sub>2</sub>, Z = O, Y = H

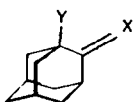
- 18 W = X = Z = H<sub>2</sub>, Y = OAc  
19 W = X = H<sub>2</sub>, Z = H, OH, Y = H  
20 W = X = Z = H<sub>2</sub>, Y = CO<sub>2</sub>H  
21 W = X = Z = H<sub>2</sub>, Y = 2'-pyridyl  
22 W = X = Z = H<sub>2</sub>, Y = 4'-pyridyl  
23 W = X = Z = H<sub>2</sub>, Y = CO<sub>2</sub>N<sub>5</sub>



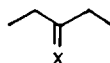
- 24 X = Y = H<sub>2</sub>, Z = H  
25 X = O, Y = H<sub>2</sub>, Z = H  
26 Y = O, X = H<sub>2</sub>, Z = H  
27 X = Y = H<sub>2</sub>, Z = OH  
28 X = Y = H<sub>2</sub>, Z = OOH

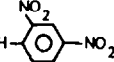


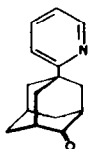
- 29 X = Y = H<sub>2</sub>, Z = H  
30 X = O, Y = H<sub>2</sub>, Z = H  
31 Y = O, X = H<sub>2</sub>, Z = H  
32 X = Y = H<sub>2</sub>, Z = OH  
33 X = Y = H<sub>2</sub>, Z = OOH



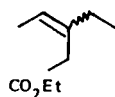
- 34 X = H<sub>2</sub>, Y = H  
35 X = O, Y = H  
36 X = H, OH, Y = H  
37 Y = OH, X = H<sub>2</sub>  
38 X = H<sub>2</sub>, Y = 2'-pyridyl  
39 X = H<sub>2</sub>, Y = 4'-pyridyl



- 40 X = CHCH<sub>3</sub>  
41 X = O  
42 X = N-NH-  
43 X = CH-CO<sub>2</sub>Et  
44 X = CH<sub>2</sub>-CO<sub>2</sub>H  
45 X = CH<sub>2</sub>-CO<sub>2</sub>Et



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Table 1. Chemical and Electrochemical Oxidations of 1, 5, 11, 24, 29 and 34 in Pyridine.

Substrate (mmol.)	Reaction Conditions & Analysis	Q(C) <sup>b</sup>	Oxygenated Products ( $\mu$ mol)		Total Oxygenated Products (mmol.)	one/ol <sup>c</sup> n <sup>d</sup>	C <sup>2</sup> /C <sup>3</sup> <sup>e</sup>	Pyridine Hydrocarbon Coupled Products (mmol.)
			2	3				
1 (50)	C (a)		2 (3150), 3 (450)		3.60	7.0	34	
1 (93)	E (a)	2000 3000	2 (2700), 3 (400) 2 (4200), 3 (600)		3.10 4.80	6.75 7.0	59 58	
5 (50)	C (a)	3000	6 (380), 7 (trace), 8 (295), 9 (640) 6 (855), 7 (180), 8 (160), 9 (540), 10 (1590)		1.60 3.32	- 7.75	14.5 <sup>g</sup> 34.8 <sup>g</sup>	<0.01 -
11 (89)	C' (a)		12 (80), 13 (230), 14 + 15 (60), 16 (35)		0.40	5.15	3.6	-
11 (89)	E' (a)	1000 2000 3000	12 (140), 13 (440), 14 + 15 (100), 16 (43) 12 (260), 13 (690), 14 + 15 (235), 16 (80) 12 (420), 13 (970), 14 + 15 (320), 16 (110)		0.73 1.26 1.82	5.8 4.05 4.35	25.1 21.4 20.6	11 15.8 14.8 15.5
24 <sup>f</sup> (50)	C (B)	1000	25 (320), 26 (1390), 27 (350), 30 (1290), 32 (540)		3.89	>10 <sup>d</sup>	34.5 <sup>h</sup>	3.37
24 <sup>f</sup> (50)	E (B)	2000 3000	25 (240), 26 (560), 27 (200), 30 (330), 32 (280) 25 (490), 26 (1080), 27 (220), 30 (690), 32 (370) 22 (780), 26 (1500), 27 (240), 30 (960), 32 (380)		1.61 2.85 3.86	- - -	52.9 <sup>h</sup> 49.3 <sup>h</sup> 45.6 <sup>h</sup>	2.35 3.83 5.22
29 <sup>f</sup> (50)	C (B)	1000	27 (40), 30 (775), 31 (810), 32 (55)		1.68	-	16.3 <sup>h</sup>	16.7
29 <sup>f</sup> (50)	E (B)	2000 3000	27 (-), 30 (405), 31 (360), 32 (35) 27 (-), 30 (865), 31 (830), 32 (50) 27 (55), 30 (1870), 31 (1725), 32 (85)		0.80 1.75 3.33	- - -	30.2 <sup>h</sup> 33.2 <sup>h</sup> 42	21.8 33.9 22.8
34 (2)	C (a)		35 (290), 36 (20), 37 (20)		0.33	14.5	3.1	38 (0.08), 39 (0.11)
34 <sup>f</sup> (14.7)	E'' (a)	1000 3000	35 (340), 36 (55), 37 (15) 35 (820), 36 (160), 37 (30)		0.41 1.01	6.2 5.1	14.5 11.8	47 (0.03) 38 + 39 + 47 (0.308)

a) C = chemical oxidation: iron cluster Fe<sub>3</sub>O<sub>4</sub>(OAc)Py<sub>3</sub> (20 mg, 2.5x10<sup>-2</sup> mmol.), zinc powder (1.31 g, 20 atm), acetic acid (3 ml), water (2 ml), under airt. 20 h., 20-30°C; C' = as C except *o*-picolinic acid (4.9 g, 4.0 mmol.) instead of acetic acid; E = electrochemical oxidation: iron cluster Fe<sub>3</sub>O<sub>4</sub>(OAc)Py<sub>3</sub> (20 mg, 2.5x10<sup>-2</sup> mmol.), pyridine (30 ml), water (3 ml), trifluoroacetic acid (3 ml), stream of oxygen, 20-30°C, current density 8 mA/cm<sup>2</sup>, cathode mercury, anode platinum plate; E' = the same as E except *o*-picolinic acid (4.9 g, 4.0 mmol.) replaced trifluoroacetic acid; E'' = the same as E except no water and current density 16 mA/cm<sup>2</sup> for the significance of (d), (E), (F), and (G) see Experimental Part.

b) 0 = total electricity passed in C (1 faraday = 96500 C); in the chemical oxidations (20 atm) is considered to give two-electrons i.e. 40 x 10<sup>-3</sup> faraday = 3685 C.

c) one/ol = total ketones/total secondary alcohols.

d) The coulombic yield n<sup>d</sup> = (4 x moles of ketones + 3 x moles of aldehyde + 2 moles of alcohols) x  $\frac{96500}{Q}$  in the case of chemical oxidations 0 = 3685 C.

e) C<sup>2</sup>/C<sup>3</sup> is defined as: total oxygenated products at secondary positions/total of tertiary alcohols. With 3-ethylpentane 5 a statistical attack would give C<sup>2</sup>/C<sup>3</sup> = 6; methylcyclopentane 11, decalines 24 and 29 would give 8 and adamantane 34, 3. f) Calculated by not taking diethylketone 41 into account. g) Calculated by assuming that diethylketone 41 necessitates 4 electrons for its formation. h) A close approximation as secondary alcohols were oxidised to ketones by the Jones reagent (see Experimental). The ratio secondary alcohols/ketones is inferior to 0.1.

i) Limit of solubility. j) Difficulties were initially encountered with the calculation of the C<sup>2</sup>/C<sup>3</sup> ratio because some peaks due to the four secondary alcohols superimposed on those due to the 4,5 tertiary alcohol 27 and the two decalones 28 and 30 in the g.c. chromatogram. This was overcome by Jones oxidation of the secondary alcohols to ketones (see Experimental).

k) The structure was confirmed by co-injection with an authentic sample of 41 and by comparison of the m.p. and <sup>1</sup>H n.m.r. of the isolated DMP derivative with that of an authentic sample m.p. 153-155°C; lit. 156°C.

an even higher efficiency. Coulombic yields in excess of 50% can be achieved when the substrates are used in large excess as for example in the case of cyclohexane. To our knowledge the only report directly relevant to our work about the oxidation of saturated hydrocarbons (cyclohexane) by means of a cathodic source of electrons in the presence of dioxygen and an iron catalyst, mentioned a low coulombic yield (7%).<sup>26</sup> This contrasts with the satisfactory efficiency obtained with aromatic hydrocarbons.<sup>6b</sup>

Full details of recent developments using the electrochemical approach will be described in due course.<sup>6a</sup>

In this paper we wish to report a comparative study of the chemical and electrochemical systems applied to simple saturated hydrocarbons possessing secondary, tertiary and, in two cases, primary C-H bonds, namely cyclohexane 1, 3-ethylpentane 5, methylcyclopentane 11, *cis*- and *trans*-decalin 24, 29 and adamantane 34. A substantial section is devoted to the search for an alternative, less expensive solvent than pyridine. For this purpose, methanol, ethanol, isopropanol and chiefly acetone, as solvents or co-solvents were examined.

The preparation of those authentic samples which are not commercially available is detailed in the experimental of this paper.

## Results

The electrochemical oxidations were performed in a one compartment cell at an imposed current density ranging from 15 to 20 mA/cm<sup>2</sup>. The potential is then "self-adjusted" by the reduction of the first reducible species of the medium, i.e. molecular oxygen which is supplied by simply bubbling a constant flow of oxygen gas through the solution.<sup>5</sup> The carboxylic acids used were trifluoroacetic, acetic and  $\alpha$ -picolinic acids, the latter was found to be effective in the electrochemical system as well.<sup>4</sup> Chemical oxidations were carried out according to the  $\text{Cr}^{\text{IV}}$  procedure.<sup>3</sup> In both the chemical and electrochemical systems, reaction mixtures were analysed and compared with authentic samples by G.L.C.

### *Chemical and Electrochemical Oxidations in Pyridine.*

The oxidations of cyclohexane 1, adamantane 34, methylcyclopentane 11, 3-ethylpentane 5, *cis*- and *trans*-decalins 24 and 29 afforded the results listed in Table 1.

Cursory examination of Table 1 will reveal that electrochemical and chemical oxidation of the same substrate gives approximately the same results confirming what had already been noted in some of our previous observations.<sup>4,5</sup> Ketones are always the major products and it is particularly worthy to note that selectivities evaluated by the *one/ol* and  $\text{C}^2/\text{C}^3$  ratios are quite similar for both systems. We had previously<sup>4</sup> determined the content of pyridine-hydrocarbon coupled products formed by attack of tertiary carbon radicals on pyridine (or protonated pyridine) for low concentrations of adamantane 34 and *trans*-decalin 29. This reaction was shown to be in competition with the capture of dioxygen by the tertiary adamantyl radical.<sup>3</sup> Examination of Table 1 indicates that adamantane 34 behaves anomalously in the sense that it gives a higher quantity of coupled products 38, 39 and 47 whereas cyclohexane 1, *cis* (24) and *trans* (29) decalins afforded comparatively small amounts of this type of compounds which could not even be detected in oxidation of methylcyclopentane 11 and 3-ethylpentane 5.

In the electrochemical system the coulombic yield  $\eta$  (calculated as indicated in footnote d of Table 1) is usually higher than that of the chemical system for a comparable quantity of electricity (i.e. = 3865 C). Moreover, with the exception of 3-ethylpentane 5, the reaction was monitored by analysing aliquots taken at every 1000 C. The steadiness of the  $\eta$  values indicates that the oxidation process maintains its efficiency throughout the electrolysis. This in effect means that over-oxidation of ketones and alcohols does not occur to appreciable

extent, and that a greater amount of substrate could be oxidised by passing more current through the mixture. Conversely, low coulombic yields  $\eta$  could either be due to a competitive over-oxidation of oxygenated products (calculation of  $\eta$  takes only the amounts of alcohols and ketones formed into account) or to a consumption of electrons in useless side reactions. We have previously isolated bipyridines in large amounts (ca. 100–150 mg) from the mixtures obtained in the chemical oxidation.<sup>3</sup>

The formation of these bipyridines was explained by the reduction and coupling of pyridine.<sup>3</sup> In the electrochemical system the potential of the cathode ( $\approx -0.7$  V vs SCE) is not sufficient to reduce pyridinium cations to any great extent.<sup>6a</sup> Only a small quantity of bipyridines (ca. 20 mg) were isolated from the basic fraction of the mixtures. This rules out the hypothesis that pyridine consumes electrons in bipyridine formation–reduction. Even if one considers the pyridine–hydrocarbon coupled products the overall  $C^2/C^3$  ratios are much higher than typical values for a radical reaction. Recently,  $C^2/C^3$  ratios of 0.14 and 0.40 were reported for adamantane 34<sup>7</sup> and cis-decalin 24<sup>8</sup> radical type oxidations respectively.

*Electrochemical and Chemical Oxidations in Pyridine - co-solvent Mixtures and in Acetone.*

During our studies in the  $Glf^{IV}$  system numerous experiments have shown that the replacement of the pyridine by other solvents, including those closely related to it in structure, led to a diminution in the regioselectivity for methylene activation.<sup>3,9</sup> However, owing to its cost the search for solvents which could at least satisfactorily replace some of the pyridine was nonetheless pursued. Because of the relative inertness of our systems towards inter alia alcohols and ketones we, at first, chose to replace half of the amount of pyridine by oxygenated solvents (Table 2).

Table 2. Electrochemical Oxidation of Cyclohexane 1 in Pyridine + co-solvent.

<u>1</u> + $CF_3CO_2H$ + $Fe_3O_4(OAc)_6Pyr_{3,5}$ + Pyridine + Y		$O_2$ / cathode Hg		one-compartment system		
10 ml (93 $\mu$ mol)	3 ml	$2.5 \times 10^{-2}$ mmol.	15 ml	15 ml	$i_c$ 16 mA/cm <sup>2</sup> , T 20–30°C	<u>2</u> + <u>3</u>
Y	Q(C) <sup>a</sup>	<u>2</u> (mmol)	<u>3</u> (mmol)	Total Oxygenated <sup>c</sup> Products (mmol)	one/ol	$\eta$ %
MeOH	1000	0.62	0.14	0.76	4.4	27
	2000	1.16	0.33	1.49	3.5	26
EtOH	1000	0.82	0.25	1.07	3.3	36
	2000	1.27	0.27	1.54	4.7	27
iPrOH	1000	0.80	0.24	1.04	3.3	36
	2000	1.34	0.46	1.80	2.9	30
acetone	1000	1.27	0.40	1.67	3.2	57
	2000	2.75	0.76	3.51	3.6	60
pyridine	2000	2.71	0.38	3.09	7.1	56
	3000	4.20	0.59	4.79	7.1	58

a,b): see footnotes b), d) of the Table 1.

c): aliquots were analysed according to procedure (a) (see Experimental Part).

Replacement of this quantity of pyridine in the electrochemical system by either methanol, ethanol or isopropanol results in diminished overall yields and a lower selectivity (measured by the one/ol ratio). The coulombic yield  $\eta$  is also lower than that of the standard experiment. On the contrary, acetone as co-solvent slightly increases the overall yield, maintains the coulombic yield but the one/ol ratio is lower than in pyridine.

Far from being discouraging these results prompted us to study the electrochemical oxidation of cyclohexane 1 and other substrates viz. adamantane 34, methylcyclopentane 11, 3-ethylpentane 5, cis- and trans-decalins 24 and 29 in acetone.

Comparison of Tables 1 and 3 reveals that electrochemical oxidation of 1, 34, 11, 5, 24 and 29 in acetone gives a different distribution of the same compounds in approximately the same overall yield as in pyridine. The selectivity for ketone formation, as measured by one/ol and  $C^2/C^3$  ratios, is in each case much lower in acetone.

Interestingly enough, the oxidation of methylcyclopentane 11 in acetone tends to depend on the carboxylic acid used. Because this observation seemed surprising we decided to perform further experiments to bring additional informations. First, it was demonstrated that tertiary acetate 18 is not formed by any acetylation of the tertiary alcohol 16 under the reaction conditions during the electrolysis or by a parallel chemical reaction. Evidently, the acetate 18 must derive from a tertiary carbonium ion trapped by acetic acid. Although literature data<sup>25</sup> left no doubt about the difficulty to carry out a two-electrons anodic oxidation of the tertiary C-H bond in the case of the relatively unstrained methylcyclopentane 11, we undertook to verify this hypothesis. For this purpose we used the two-compartment electrochemical cell that we previously described.<sup>4</sup> Methylcyclopentane 11 in wet pyridine (or acetone) - acetic acid mixtures is not oxidised at the anode to either alcohol 16 or acetate 18 at a potential lower than +3.5 V vs. S.C.E. An explanation as to the formation of 18 could be that methylcyclopentane initially give an iron-carbon  $\sigma$  bond intermediate postulated previously in the chemical system.<sup>3</sup> The same intermediate was also invoked in the electrochemical system,<sup>5</sup> as the result of an iron-catalysed cathodic process. In the one-compartment system, this organo-iron species would have sufficient life-time to diffuse, at least partly, to the anode where it could be oxidised to the corresponding carbocation. Further work is obviously needed to clarify this intriguing observation. That no tertiary trifluoroacetate is formed when trifluoroacetic acid is used instead of acetic acid could be due to the lower nucleophilicity of  $CF_3CO_2H$  as compared to  $CH_3CO_2H$ , or to the instability of the trifluoroacetate under these conditions. It is noteworthy that the total amounts of tertiary oxidised products in AcOH and  $CF_3CO_2H$  are comparable in both cases.

On the contrary, it is not surprising<sup>25</sup> to observe an anodic oxidation with adamantane in acetone (Table 3). Because of the absence of pyridine which is more oxidisable at the anode than the saturated hydrocarbon, the oxidation of the weaker tertiary C-H bond to give a carbon radical followed by further oxidation to the corresponding carbocation explains the regioselectivity observed in favour of the tertiary alcohol 37 under these conditions.

Table 3. Electrochemical Oxidations of 1, 5, 11, 24, 29 and 34 in Acetone.

Substrate (mmol.)	Reaction Conditions & Analysis	Q(C) <sup>b</sup>	Oxygenated Products (μ mol)	Total Oxygenated Products (mmol.)	one/ol <sup>c</sup>	η <sup>d</sup>	C <sup>2</sup> /C <sup>3</sup> <sup>e</sup>
<u>1</u> (93)	E <sup>III</sup> (α)	2000	<u>2</u> (960), <u>3</u> (2160)	3.12	0.44	39	
<u>5</u> (50)	E <sup>III</sup> (α)	1060	<u>6</u> (400), <u>7</u> (280), <u>8</u> (445), <u>9</u> (trace), <u>41</u> (560)	1.68	1.42 <sup>g</sup>	48 <sup>j</sup>	1.53 <sup>g</sup>
		2000	<u>6</u> (620), <u>7</u> (330), <u>8</u> (550), <u>9</u> (trace), <u>41</u> (710)	2.21	1.87 <sup>g</sup>	34 <sup>j</sup>	1.73 <sup>g</sup>
		3000	<u>6</u> (495), <u>7</u> (250), <u>8</u> (380), <u>9</u> (trace), <u>41</u> (670)	1.80	1.98 <sup>g</sup>	19 <sup>j</sup>	1.96 <sup>g</sup>
<u>11</u> (89)	E <sup>IV</sup> (δ)	2000	<u>12</u> (85), <u>13</u> (240), <u>14</u> + <u>15</u> (125), <u>16</u> (330), <u>18</u> (315)	1.10	2.60	13.7 <sup>f</sup>	0.70 <sup>f</sup>
		3000	<u>12</u> (160), <u>13</u> (445), <u>14</u> + <u>15</u> (273), <u>16</u> (630), <u>18</u> (500)	2.17	2.20	16.8 <sup>f</sup>	0.78 <sup>f</sup>
<u>11</u> (220)	E <sup>III</sup> (α)	3000	<u>12</u> (290), <u>13</u> (310), <u>14</u> + <u>15</u> (380), <u>16</u> (1330)	2.31	1.58	18.7	0.74
<u>24</u> (50)	E <sup>III</sup> (γ)	1050	<u>25</u> (85), <u>26</u> (490), <u>27</u> (250), <u>30</u> (290), <u>32</u> (380)	1.50	-	35 <sup>b</sup>	1.37
		1990	<u>25</u> (180), <u>26</u> (675), <u>27</u> (355), <u>30</u> (445), <u>32</u> (600)	2.25	-	28 <sup>b</sup>	1.36
		3080	<u>25</u> (420), <u>26</u> (850), <u>27</u> (455), <u>30</u> (550), <u>32</u> (810)	3.09	-	25 <sup>b</sup>	1.44
<u>29</u> (50)	E <sup>III</sup> (γ)	1070	<u>27</u> <sup>i</sup> (25), <u>30</u> (220), <u>31</u> (430), <u>32</u> (38)	0.71	-	18.7 <sup>h</sup>	10.3
		2000	<u>27</u> <sup>i</sup> (30), <u>30</u> (260), <u>31</u> (680), <u>32</u> (50)	1.02	-	14.4 <sup>h</sup>	11.7
		3000	<u>27</u> <sup>i</sup> (45), <u>30</u> (320), <u>31</u> (910), <u>32</u> (70)	1.35	-	12.6 <sup>h</sup>	10.7
<u>34</u> (2)	E <sup>III</sup> (α) <sup>k</sup>	2000	<u>35</u> (12), <u>36</u> (42), <u>37</u> (280)	0.33	0.28	6	0.2

a) E<sup>III</sup> = Electrochemical oxidation: iron cluster Fe<sub>3</sub>O(OAc)<sub>6</sub>Pyr<sub>3.5</sub> (20 mg, 2.5 × 10<sup>-2</sup> mmol), acetone (30 ml), water (3 ml), trifluoroacetic acid (3 ml), stream of oxygen, 20–30°C, current density 16 mA/cm<sup>2</sup>, cathode mercury, anode platinum plate, E<sup>IV</sup> = the same as E<sup>III</sup> except that acetic acid (3 ml) replaced trifluoroacetic acid, and tetraethylammonium tetrafluoroborate (0.64 g, 2.95 mmol) was added.

f) Calculated by considering the tertiary acetate 18 as a tertiary alcohol.

g) Calculated by not taking diethylketone 41 into account.

h) Calculated by assuming that half the quantity of ketones given in the Table were initially secondary alcohols. This is a fair assumption based on the inspection of g.l.c. chromatogram prior to Jones oxidation.

i) Calculated by assuming that the ratio of 27 to 32 is 0.62.

j) see footnote g) of the Table 1.

k) Anodic oxidation performed in a two compartment electrochemical cell, <sup>4</sup>Et<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> as supporting electrolyte; anodic potential > +2V vs. S.C.E.

#### Chemical and Electrochemical Oxidation of Cyclohexane and Adamantane in Pyridine-acetone Mixtures.

In order to gain more insight into the dependence of the selectivity on the presence of pyridine, we performed a series of experiments using increasing proportions of acetone. When the acetone/pyridine ratio is increased the total amount of oxygenated products derived from cyclohexane 1 stays more or less constant (Table 4) whereas the coulombic yield η decreases slightly. The decrease in the one/ol ratio is more accentuated and drops almost linearly with the volume fraction of pyridine. We also examined the electrochemical oxidation of adamantane 34 under the same conditions (Table 5). When the amounts of pyridine decreased the efficiency and the selectivity of the oxidation diminished, as well as the quantity of pyridine-hydrocarbon coupled products. In the total absence of pyridine, as mentioned above, the major oxidised product is the tertiary alcohol 37.

Table 4. Electrochemical Oxidation of Cyclohexane 1 in Mixtures of Pyridine and Acetone.

<u>1</u> + CF <sub>3</sub> CO <sub>2</sub> H + Fe <sub>3</sub> O(OAc) <sub>6</sub> Pyr <sub>3.5</sub>		----- <sup>O<sub>2</sub>/cathode Hg</sup> -----> <u>2</u> + <u>3</u>	
10 ml (93 mmol)	3 ml	2.5x10 <sup>-2</sup> mmol.	one-compartment system i <sub>c</sub> 16 mA/cm <sup>2</sup> , T 20-30°C Q <sub>T</sub> 2000 Cb

Acetone (ml)	Pyridine (ml)	2 (mmol)	3 (mmol)	Total Oxygenated Products (mmols)	one/ol	η % <sup>a</sup>
0	30	2.71	0.38	3.09	7.1	56
15	15	2.80	0.80	3.60	3.5	62
20	10	1.70	0.84	2.54	2.0	41
25	5	1.95	1.19	3.14	1.6	49
28	2	1.60	1.62	3.22	1.0	47
29.0	1.0	1.30	2.25	3.55	0.58	47
29.5	0.5	1.17	2.25	3.42	0.52	44
30	0	0.96	2.16	3.12	0.44	39

a) see footnote d) of the Table 1.

b) see footnote c) of the Table 1.

Table 5. Electrochemical Oxidation of Adamantane 34 in Mixtures of Pyridine and Acetone.

<u>34</u> + CF <sub>3</sub> CO <sub>2</sub> H + Fe <sub>3</sub> O(OAc) <sub>6</sub> Pyr <sub>3.5</sub> + acetone + pyridine					----- <sup>O<sub>2</sub>/cathode Hg</sup> -----> <u>35</u> + <u>36</u> + <u>37</u>	
2 mmol	3 ml	2.5x10 <sup>-2</sup> mmol.	X	Y	one compartment system i <sub>c</sub> 16 mA/cm <sup>2</sup> , T 20-30°C Q <sub>T</sub> 2000 Cb	

X (ml)	Y (ml)	35 (%)	36 (%)	37 (%)	Total oxygenated Products (%)	C <sup>2</sup> /C <sup>3</sup> <sup>c</sup>	η <sup>d</sup>	one/ol <sup>e</sup>	recovered 34 (%)	38 + 39 + 47 (%)
0	30	13.0	1.60	0.4	15.0	37	5.2	8.1		
5	25	10.2	1.9	0.3	12.4	40	4.4	5.4	67	14
10	20	11.25	2.0	0.55	13.8	24	4.8	5.6	69	
15	15	7.30	2.35	0.60	10.25	16	3.4	3.1	75	5
20	10	5.00	2.5	0.40	7.90	18	2.4	2		
25	5	3.50	2.05	0.50	6.05	11	1.8	1.7		
27.5	2.5	1.50	1.07	1.2	3.77	2	1.0	1.4	91	2.2
30 <sup>a</sup>	0	0.6	2.10	14.0	16.7	0.2	6	0.3		
30 <sup>b</sup>	0	1.25	0.70	9.9	11.85	0.2	4.2	1.8		
30 <sup>b</sup>	0	1.40	0.90	11.8	14.10	0.2	5.0	1.3		

a) 2 ml of H<sub>2</sub>O were added to ensure conductivity and the total electricity was 1200 Cb.

b) 0.7 g of Et<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> were added and the total electricity was 1200 Cb.

c) see footnote e) of Table 1.

d) see footnote d) of Table 1.

e) see footnote c) of Table 1.



The partial replacement of pyridine by acetone was also studied in the chemical system. The results given in Table 6 show that the selectivity ( $C^2/C^3$ ) continuously decreases whereas the recovered hydrocarbon increases when the volume ratio of acetone increases. Interestingly, the overall yield maintains more or less constant until half of the pyridine is replaced by acetone.

Table 6. Chemical Oxidation of Adamantane 34 in Mixtures of Pyridine and Acetone.

						air	
$\underline{34}$ + Zn + AcOH + Fe <sub>3</sub> O(OAc) <sub>6</sub> Pyr <sub>3.5</sub> + acetone + pyridine						$\xrightarrow{20-30^\circ\text{C}, 12 \text{ h}, \text{H}_2\text{O} (2 \text{ ml})}$	
2 mmol. 20 mgat. 40 mmol. 2.5x10 <sup>-2</sup> mmol. X ml Y ml							
X (ml)	Y (ml)	<u>37</u> (%)	<u>36</u> (%)	<u>35</u> (%)	Total oxygenated Products (%)	$C^2/C^3$ <sup>a)</sup>	Recovered <u>34</u> (%)
0	28	0.85	0.75	16.2	17.8	19.9	47.7
10	18	1	0.6	14.55	16.15	15.15	47.35
14	14	1.9	0.65	14.0	16.55	7.7	60.4
18	10	3.2	0.3	7.6	11.10	2.45	78
23	5	2.6	-	3.6	6.2	1.38	95.4
28	0	0.6	0.2	<0.1	0.8	-	

a) see footnote e) of Table 4.

### Discussion

The results reported in this paper clearly confirm the parallel behaviour displayed by both the chemical and electrochemical systems in pyridine as well as in acetone. In the electrochemical oxidations higher coulombic yields are consistently reached than in the chemical system and, moreover, this coulombic yield tends to remain constant throughout the course of electrolysis. Better conversions could be achieved simply by prolonging the duration of electrolysis or by improving the characteristics of the electrochemical apparatus.

In previous papers,<sup>2,3</sup> we demonstrated that in the chemical system, in pyridine as solvent, the formation of oxidised products at secondary and tertiary positions of adamantane 34 was not influenced by the same factors. We came to the conclusion that a radical mechanism was, at least in part, involved in the formation of tertiary products, mainly on the basis of the observed competition between dioxygen and pyridine. For the secondary position where such a competition is not observed, a different mechanism, essentially non-radical in nature, was proposed. The secondary alcohol would then come from the insertion of oxygen into a  $\sigma$  Fe-C bond. The major oxidised product (ketone) would derive from a hypothetical iron-carbene<sup>3</sup> formed from the same Fe-C intermediate. The oxidation of both cis- and trans-decalins 24 and 29 was ideal to carry out an in-depth examination of the mechanism of tertiary alcohol formation, i.e. 27 and 32. Non-catalysed auto-oxidations of both cis- and trans-decalins 24 and 29 were performed by simply bubbling air through the respective hydrocarbons at 110°C<sup>10</sup> followed by trimethylphosphite reduction. It was

observed that cis-decalin 24 consistently gives a greater amount (10-12 times) of the tertiary alcohols 27 and 32 than does trans-decalin 29 irrespective of the type of oxidation performed, be it chemical or electrochemical in acetone or pyridine, or auto-oxidation. We believe that the explanation lies in steric rather than in bond strength arguments. As a consequence, the high  $C^2/C^3$  values for the oxidation of trans-decalin 29 could be interpreted by the relative inaccessibility of its tertiary C-H bond to attack by the active species. Furthermore, the trans/cis tertiary alcohol ratio 32/27 remains approximately constant in whichever conditions tested. Recently, cobalt catalysed oxidation of cis-decalin was studied.<sup>8</sup> This radical process gave mainly cis and trans tertiary alcohols ( $C^2/C^3 \approx 0.4$ ) with a somewhat different trans/cis ratio (3.6) than that observed by ourselves (1.3-1.9). Because of the similarities of the oxidations performed under both the iron-catalysed (chemical or electrochemical systems) and non-catalytic conditions (auto-oxidation), we think that in cis- and trans-decalin the formation of the tertiary iron-carbon  $\sigma$ -bond evolves largely to give a carbon radical which naturally gives the same ratio of cis- and trans- products as does auto-oxidation.

In order to establish the provenance of the diethylketone 41 in the oxidation of 3-ethylpentane 5 two blank experiments were carried out. It was found that a  $Gif^{IV}$  experiment on triethylcarbinol 8 (7 mmoles) gave approximately 4% of the ketone 41. The same ratio of 3-ethyl-pent-2-ene 40 was also converted to the ketone 41 under identical conditions. Cleavages of  $\sigma$  C-C bonds have already been observed in cholestane derivatives<sup>11</sup> and in the  $Gif^{IV}$  oxidation of (+) tetrahydrolinalool.<sup>1</sup>

Electrochemical oxidations performed in acetone or in pyridine co-solvent mixtures proceed satisfactorily. Although the same oxygenated products are obtained in all these solvent systems, their distribution is quite different. Thus far, the results obtained agree in ascribing a unique role to pyridine in enhancing the regioselectivity in favour of methylene activation.

In recent publications Prof. A.E. Shilov, Dr. Yu.V. Geletii and their colleagues<sup>12</sup> have reported on their own work on the  $Gif$  and  $Gif$ -Orsay systems. They have repeated many of the experiments that we have described<sup>2,3,9</sup> and have obtained similar results. The selectivity of attack on secondary positions and the non-radical nature of the reaction in its early stages have been confirmed. Thus addition of ethanol and of acetaldehyde does not inhibit the reaction. The difference between pyridine and acetone in the oxidation of cyclohexane has also been observed by our Soviet colleagues as due to the formation of ketone and secondary alcohol by two different routes.

Shilov *et al.*<sup>12</sup> have made the ingenious suggestion that the oxidising agent in the  $Gif$  and  $Gif$ -Orsay systems is not an iron species, but a radical cation formally derived by electron removal from pyridine-N-oxide. The iron catalyst which we introduced provides a special mechanism to convert pyridine into this radical cation species. We await with interest further news of this research.

## Experimental

Unless otherwise stated, <sup>1</sup>H n.m.r. spectra were recorded on a Varian EM 360 (60 MHz) or Bruker (200 MHz) instrument using deuterated chloroform as solvent and tetramethyl-silane as internal standard. Melting points are uncorrected and were determined with a Reichert Thermovar hot-stage apparatus. I.R. Spectra were recorded on a Perkin-Elmer 457 instrument. Mass spectra were recorded on AEI MS 9 and MS 50 instruments. Column chromatography was carried out on silica 60 (Merck) while preparative layer chromatography was performed on glass plates coated with Kieselgel F 1500 LS-254, Schleicher & Schüell. Analytical g.l.c. employed either a Girdel series 300 gas-chromatograph with both 1.5 and 4 m long columns OV 17 5% (chromosorb WAWDMCS), or a Carlo Erba series 2150 instrument equipped with an OV 225 5% (chromosorb WHP) 5 m long column, or an OV 17 3% (gaz chrom Q) 5 m long column. The columns were employed as described below for the respective substrates.

(i) For the oxidation of cis and trans-decalin 24 and 29. - Column OV 17, 3%, 4 m; temperature programme : 100-190°C (2°C/min); detector and injector temperature : 200°C; retention times (seconds) : cis-decalin 24: 1122, trans-decalin 29: 892; tetralin (internal standard) 1536, cis-decal-9-ol 27: 1998, trans-decal-9-ol 32: 1773, the secondary alcohols between 1950 and 2300, cis-decal-1-one 25: 2354, trans-decal-1-one 30: 2279, cis-decal-2-one 26: 2568, trans-decal-2-one 31: 2334.

(ii) For the oxidation of 3-ethylpentane 5. - Column OV 225, 3%, 5 m; temperature programme : isothermal at 70°C for 18 min, then increased at a rate of 2°C/min to 145°C; retention times (seconds) : 3-ethyl-pentane 5: 332, 3-ethyl-pent-2-ene 40: 363, pentan-3-one 41: 640, 3-ethyl-pentan-2-one 6: 1219, 3-ethyl-pentan-3-ol 8: 1347, 3-ethyl-pentanal 9: 1436s, 3-ethyl-pentan-2-ol 7: 1636s, adamantane 34 (internal standard): 2027 and 3-ethyl-pent-1-ol 10: 2225.

(iii) For the oxidation of methylcyclopentane 11. - Column OV 17, 5%, 4 m; temperature programme : 70-160°C (2°C/min), injector and detector temperatures : 250°C; retention times (seconds) : 1-methylcyclopentan-1-ol 16: 640, the secondary alcohols between 815 and 830, cyclopentane carboxaldehyde 17: 918, 2-methylcyclopentanone 12: 960, 3-methylcyclopentanone 13: 1020s, cyclopentanemethanol 19: 1120, 1-acetoxy-1-methylcyclopentane 18: 1185 and adamantane 34 (internal standard): 1685.

(iv) For the oxidation of adamantane 34. - Column OV 17, 3%, 1.5 m; temperature programme : 90-140°C (2°C/min); injector and detector temperature 250°C; retention time (seconds) : adamantane 34: 360, adamantan-1-ol 37: 970, adamantan-2-ol 36: 1190 and adamantanone 35: 1300. Naphthalene was used as internal standard.

(v) For the oxidation of cyclohexane 1. - Column OV 17, 3%, 5 m; temperature programme : 100°C (isothermal); injector and detector temperatures : 250°C; retention times (seconds) : cyclohexanol 3: 622, cyclohexanone 2: 803, adamantane 34: (internal standard).

For all hydrocarbons that were analysed the carrier gas was N<sub>2</sub> at a pressure of 1 bar. All the reagents and solvents used were commercial analytical grade unless otherwise stated.

#### Preparation of 3-ethylpentane 5 and authentic samples.

The following starting materials and authentic samples not commercially available were prepared as described below :-

3-Ethylpentane 5 was obtained by dehydration<sup>13</sup> of 8 under acid conditions (p-toluene sulphonic acid)<sup>14</sup> and subsequent hydrogenation (Pd over charcoal) of the resulting 3-ethyl-pent-2-ene 40.

3-Ethylpent-2-one 6 was prepared by decarboxylative hydrolysis<sup>15</sup> (barium hydroxide) of ethyl-2,2'-diethyl-3-oxo-butanoate. Reduction of this ketone 6 with sodium borohydride afforded 3-ethylpentan-2-ol 7.

Horner-Emmons condensation of triethylphosphonoacetate with diethylketone 41 gave a mixture of E and Z ethyl-3-ethyl-pent-3-enoate 43 and ethyl-3-ethyl-pent-2-enoate 51 which was hydrogenated over platinum oxide affording ethyl-3-ethyl-pentanoate 45. The latter in turn furnished 3-ethyl-pentan-1-ol 10 by lithium aluminium hydride reduction. The corresponding aldehyde 9 was obtained by pyridinium chlorochromate oxidation of the alcohol 10.

#### 3-Ethylpent-2-ene 40.

Triethylcarbinol 8 (84.2 g, 0.725 mol) was distilled in the presence of molecular sieves (4A) and para-toluene sulphonic acid (ca. 1 g). Care was taken to keep the distilling vapors, an azeotrope of water and the product, at a temperature of about 80°C. The upper layer containing alkene was decanted from the water of the biphasal distillate and redistilled from p-toluene sulphonic acid to remove all traces<sup>3</sup> of triethylcarbinol 16 that might have distilled over. The known 3-ethyl pent-2-ene 40<sup>3</sup> was recovered as a colourless

oil (49.8 g, 70%);  $\delta$  (60 MHz,  $\text{CDCl}_3$ ): 0.98 (3H, t, J 7 Hz,  $\text{CH}_3\text{CH}_2$ ), 1.00 (3H, t, J 7 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.58 (3H, d, J 7 Hz,  $\text{CHCH}_3$ ) and 5.08 (1H, q, J 7 Hz,  $-\text{CH}$ ); m/z: 98 ( $\text{M}^+$ , 39), 97 (17), 83 (14), 71 (16), 70 (38), 69 (100), 56 (22), 55 (72) and 54 (51%).

### 3-Ethylpentane 5.

Neat 3-ethyl pent-2-ene 40 (7.25 g, 73.8 mmol) and 10% palladium on carbon (80 mg) were stirred at room temperature under hydrogen (60 bars). The reaction was monitored both by  $^1\text{H}$  n.m.r. (disappearance of the vinylic proton at  $\delta$  5.08 ppm) and by g.l.c. After 30 hours the catalyst was filtered off, affording 3-ethyl pentane 5 as a liquid (5.44 g, 74%). The liquid products obtained from successive runs were accumulated and distilled prior to use (b.p. 96-98°C, 760 mmHg);  $\delta$  (60 MHz,  $\text{CDCl}_3$ ): 0.85 (9H, t, J 6 Hz,  $-\text{CH}_3$ ), 1.03-1.78 (7H, m,  $-\text{CH}$  and  $\text{CH}_2$ ); m/z: 100 ( $\text{M}^+$ , 6.7), 71 (75), 70 (100), 69 (41), 55 (22) and 54 (17%).

### 3-Ethylpentan-2-one 6.

Ethyl 2,2-diethyl-3-oxo-butanoate (2.0 g, 10.7 mmol) prepared by the alkylation of ethyl 3-oxo-butanoate by the method of Frankland and Duppa<sup>15</sup> was refluxed for 18 hours in an aqueous solution of barium hydroxide<sup>15,16</sup> (10% w/v, 200 ml). The solution was decanted and extracted with ether (3x100 ml). The combined ethereal extracts were washed twice with saturated aqueous  $\text{NaHCO}_3$ , dried ( $\text{MgSO}_4$ ) and evaporated affording a yellow oil which was distilled on a cold finger to give the known 3-ethylpentan-2-one 6 as a fragrant, colourless oil (466 mg, 38%);  $\delta$  (60 MHz,  $\text{CDCl}_3$ ): 0.88 (6H, t, J 7 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.5 (4H, q, J 7 Hz,  $\text{CH}_2$ ), 2.13 (3H, s,  $\text{CO}-\text{CH}_3$ ) and 2.37 (1H, m,  $\text{CH}-\text{CO}$ ); m/z: 114 ( $\text{M}^+$ , 6.4), 86 (24), 85 (18), 71 (31), 70 (30), 55 (12) and 54 (11%).

The aqueous phase was reacidified with 1N HCl and extracted with ether (3x100 ml) which after being separated, dried ( $\text{MgSO}_4$ ) filtered and evaporated gave 2-ethyl butanoic acid (125 mg, 10%).

### 3-Ethylpentan-2-ol 7.

3-Ethylpentan-2-one 6 (0.5 g, 4.38 mmol) was dissolved in anhydrous methanol (25 ml).  $\text{NaBH}_4$  (232 mg, 6.13 mmol) was added and stirring allowed to continue overnight. Water was then added and the mixture extracted with ether (3x50 ml). After separation from the aqueous phase, the combined ethereal layers were dried over  $\text{MgSO}_4$ , filtered and evaporated to yield the known title compound 7 (463 mg, 91%). An analytical sample was obtained by distilling and collecting the condensate on a cold finger;  $\delta$  (60 MHz,  $\text{CDCl}_3$ ): 0.9 (6H, t, J 5 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.15 (3H, d, J 6 Hz,  $\text{CHOH}-\text{CH}_3$ ), 1.15-1.78 (5H, m, C-H and  $-\text{CH}_2$ ), 2.94 (1H, br s, OH), and 3.8 (1H, m,  $\text{CHOH}$ ); m/z: 98 ( $\text{M}-18$ , 0.7), 71 (10), 70 (38), and 55 (16%).

### Ethyl 3-ethylpent-2-enoate 43 and Ethyl 3-ethylpent-3-enoate 46.

A pre-weighed, dry, 500 ml three-necked flask equipped with a stirrer, condenser and dropping funnel was charged with a 50% dispersion of sodium hydride and purged with dry argon. The mineral oil was removed from the sodium hydride by the repetitive addition of small volumes (ca. 5 ml) of anhydrous pentane, stirring, and subsequently removal of the pentane by means of a syringe after allowing the white powder to settle. To the dry powder (1.39 g, 58 mmol) anhydrous benzene (100 ml) was added followed by the dropwise addition of freshly distilled triethyl phosphonoacetate (13.12 g, 58 mmol) over thirty minutes. After the addition of triethyl phosphonoacetate was complete, the mixture was stirred for an hour at room temperature to ensure complete reaction (hydrogen evolution had ceased). Pentan-3-one 41 (5 g, 58 mmol) was then added dropwise to the solution which was maintained at 20-30°C by appropriate cooling with an ice bath. The mixture became viscous during this addition owing to the formation of a gummy sodium diethyl phosphate suspension, but heating the mixture at 60°C for 15 min ensured continuous stirring. The resulting product was cooled to room temperature and filtered. The gummy precipitate that remained behind in the flask was washed with several portions of hot benzene (30 ml), decanted and filtered. Benzene and any unreacted pentan-3-one were removed by distillation under reduced pressure. A mixture of ethyl-3-ethylpent-2-enoate 43 and ethyl-3-ethylpent-3-enoate 46 was isolated in an approximate<sup>17b</sup> ratio of 2:1 (7.42 g, 82%). This was employed directly in the subsequent reaction.

### Ethyl 3-ethylpentanoate 45.

The above mixture of ethyl 3-ethylpent-2-enoate 43 and ethyl 3-ethylpent-3-enoate 46 (3.00 g, 19.2 mmol) in absolute methanol (50 ml) was stirred for 3 hrs under hydrogen at atmospheric pressure in the presence of platinum oxide ( $\text{Pt}_2\text{O}$ ) (40 mg). The solution was then filtered to remove the catalyst and the methanol evaporated under reduced pressure to afford the title compound 45 (2.98 g, 98%); IR  $\nu$  (film): 1738, 1465, 1375, 1250, 1180, 1100 and 1035  $\text{cm}^{-1}$ ;  $\delta$  (200 MHz,  $\text{CDCl}_3$ ): 0.88 (6H, t, J 7 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.26 (3H, t, J 7.5 Hz,  $\text{OCH}_2\text{CH}_3$ ), 1.22-1.47 (4H, m,  $\text{CH}_2\text{CH}_3$ ), 1.75 (1H, m, J 7 Hz, CH), 2.23 (2H, d, J 7 Hz,  $\text{CH}_2\text{CO}_2\text{Et}$ ) and 4.13 (2H, q, J 7.5 Hz,  $\text{OCH}_2\text{CH}_3$ ); m/z: 158 ( $\text{M}^+$ , 0.6), 129 (6), 113 (18), 89 (13), 88 (100), 87 (38), 85 (12), 70 (27), 69 (19), 61 (24), 60 (32) and 55 (20%).  $\text{C}_9\text{H}_{18}\text{O}_2$  requires C, 68.31; H, 11.47%. Found: C, 68.14; H, 11.56%.

3-Ethylpentan-1-ol 10.

To a stirred suspension of lithium aluminium hydride (0.967 g, 25.4 mmol) in anhydrous ether (25 ml) under argon was added dropwise over 15 min a solution of ethyl 3-ethyl pentanoate 45 (2.01 g, 12.7 mmol) in anhydrous ether (50 ml). Stirring was continued at room temperature for 90 minutes after which the reaction was cooled at 0°C and aqueous saturated ammonium chloride added dropwise. Effusive bubbling ensured, and after the addition of more ether and some water (2 ml), MgSO<sub>4</sub> was added and stirring continued for an hour. The mixture was filtered and the ether removed from the filtrate under reduced pressure to afford the known alcohol 10<sup>18</sup> (1.31 g, 89%). An analytical sample was obtained by means of a micro-distillation;  $\delta$  0.87 (6H, t, J 6 Hz, CH<sub>2</sub>-CH<sub>3</sub>), 1.08-1.85 (7H, m, CH<sub>2</sub>-CH<sub>2</sub>OH, CH and CH<sub>2</sub>-CH<sub>3</sub>), 2.75 (1H, br s, OH) and 3.72 (2H, br t, J 6 Hz, CH<sub>2</sub>-OH); m/z: 98 (M-18, 4), 71 (6), 70 (60), 69 (100), 68 (47), 56 (24), 55 (34) and 54 (19%).

3-Ethylpentanal 9

To a stirred suspension of pyridinium chlorochromate <sup>19</sup> (334 mg, 1.55 mmol) in anhydrous dichloromethane (15 ml) was added a solution of 3-ethylpentan-1-ol 10 (150 mg, 1.29 mmol) in anhydrous dichloromethane (10 ml). The mixture was stirred for 1.5 hours at room temperature. It was then diluted with ether and filtered through a short pad of Florisil (ca. 3 g). The filtrate was concentrated in vacuo and the oily residue purified by preparative thin layer chromatography to give the title compound 9 (134 mg, 91%) as a volatile oil. 2,4-dinitrophenylhydrazone: m.p. 75.5-78°C (EtOH); m/z (chemical ionisation): 312 (M + NH<sub>4</sub><sup>+</sup>, 100), 295 (MH<sup>+</sup>, 77), 294 (M<sup>+</sup>, 10), 242 (16), 235 (20) and 114 (29%).

The preparation of the authentic expected products of oxidation of methylcyclopentane.

Jones oxidation of 2-methylcyclopentan-1-ol 14 gave 2-methylcyclopentanone 12 while NaBH<sub>4</sub> reduction of 3-methylcyclopentanone 13 provided an epimeric mixture of the corresponding alcohols 15. Cyclopentane carboxylic acid was reduced with lithium aluminium hydride in ether to give the primary alcohol 19, and subsequent pyridinium chlorochromate oxidation gave cyclopentane carboxaldehyde 17.

1-Methylcyclopentane carboxylic acid <sup>23</sup> (0.94 g, 7.34 mmol), prepared from cyclohexanol by the method of Koch and Haaf, <sup>22</sup> was dissolved in anhydrous dichloromethane (30 ml). Oxalyl chloride (2.80 g, 22 mmol) and N,N-dimethylformamide (2 drops) were added. The mixture was stirred overnight at room temperature after which the excess oxalyl chloride and solvent were removed under reduced pressure to give the acid chloride; this was diluted with fresh anhydrous dichloromethane (30 ml) and employed immediately. Camphorsulphonic acid (11.024 g, 47 mmol) and N-hydroxy 2-pyridinethione (1.118 g, 8.81 mmol) were dried azeotropically in toluene immediately before use and added to acid chloride solutions under argon in the dark at 0°C, followed by pyridine (4.06 g, 51.4 mmol). Stirring was continued for 30 minutes at 0°C in the dark during which a yellow colour developed due to the formation of the mixed anhydride 23. The reaction flask was then brought out into light and irradiated with a 100 W tungsten lamp for 3 hours, care being taken to maintain the temperature at 0°C. During this time the yellow colour diminished noticeably in intensity. After the disappearance of the mixed anhydride (t.l.c.) the mixture was thrown into methylene chloride and shaken a few times with saturated aqueous sodium hydrogen carbonate solution. The organic phase was dried (MgSO<sub>4</sub>), filtered and evaporated. Pyridine was removed from the residual liquid under high vacuum. The crude oil was chromatographed (eluant: chloroform-acetone 20:1, v/v) to yield the known <sup>24</sup> 1-(2'-pyridyl)-1-methylcyclopentane 21 (154 mg, 13%);  $\delta$  (60 MHz, CDCl<sub>3</sub>): 1.37 (3H, s, CH<sub>3</sub>), 1.58-2.41 (8H, m, CH<sub>2</sub>), 6.97-7.88 (3H, m, 3'-, 4'- and 5'-H) and 8.60 (1H, br d, 6'-H); m/z: 161 (M<sup>+</sup>, 11), 146 (M-15, 51), 132 (29) and 120 (100%). This was followed by di-2'-pyridyl disulphide then 1-(4'-pyridyl)-1-methylcyclopentane 22 (189 mg, 16%);  $\delta$  (200 MHz, CDCl<sub>3</sub>): 1.27 (3H, s, CH<sub>3</sub>), 1.83 (8H, m, CH<sub>2</sub>), 7.31 (2H, d, J 5 Hz, 3'- and 5'-H) and 8.59 (2H, d, Br s, w<sub>1/2</sub> 11 Hz, -2' and -6'H); m/z: 161 (M<sup>+</sup>, 100), 146 (M-15, 36), 132 (20), 120 (6) and 119 (20%).

Typical Procedures for the Gif-Orsay Electrochemical Oxidation.

The electrochemical cell comprises a mercury pool as cathode, a platinum plate as anode and a reference electrode. Oxygen gas (2 ml/min) is bubbled through the solution during the electrolysis.

In pyridine :

(E) Hydrocarbon (50 mmol), pyridine (30 ml), trifluoroacetic acid (30 ml), water (3 ml) and the iron catalyst [Fe<sub>2</sub>O(OAc)<sub>6</sub>](C<sub>6</sub>H<sub>5</sub>N)<sub>3</sub> (20 mg, 2.5x10<sup>-2</sup> mmol) were thoroughly mixed in an Erlenmeyer flask before being transferred to the electrochemical cell. A current of 15-20 mA/cm<sup>2</sup> was passed through the stirred reaction mixture at 25-30°C and aliquots taken at each 1000 Cb. Treatment of the aliquots according to (B) (see below) afforded the oxidation products which were analysed by g.l.c.

(E') The same procedure as E except that  $\alpha$ -picolinic acid (4.9 g, 40 mmol) was used instead of trifluoroacetic acid. In the case of methylcyclopentane 11, 88.8 mmoles of hydrocarbon were used.

(E'') The same procedure as E except that water was omitted.

#### In acetone

(E''') Hydrocarbon<sub>2</sub> (50 mmol), acetone (30 ml), trifluoroacetic acid (3 ml), water (3 ml) and the iron catalyst  $\text{Fe}_3\text{O}(\text{OAc})_6\text{Pyr}_{3,5}$  (20 mg,  $2.5 \times 10^{-2}$  mmol) were thoroughly mixed in an Erlenmeyer flask and transferred to the electrochemical cell. A current of 15–20 mA/cm<sup>2</sup> was passed through the stirred reaction mixture at room temperature and aliquots taken at each 1000 Cb were treated either according to procedure (a) or (γ) (see below).

(E<sup>iv</sup>) Hydrocarbon (10 ml, 88.8 mmol), acetone (30 ml), acetic acid (3 ml), tetraethylammonium tetrafluoroborate (0.64 g, 2.95 mmol) and  $\text{Fe}_3\text{O}(\text{OAc})_6\text{Pyr}_{3,5}$  (20 mg,  $2.5 \times 10^{-2}$  mmol) were mixed in an Erlenmeyer and transferred to the electrochemical cell. Aliquots taken at each 1000 Cb were treated according to procedure (a) (see below).

#### Typical Procedure for the Gif<sup>IV</sup> Chemical Oxidations.<sup>2,3</sup>

(C) Hydrocarbon (50 mmol), pyridine (30ml), acetic acid (3 ml), water (3 ml), zinc powder (1.31 g, 20 mmol) and  $\text{Fe}_3\text{O}(\text{OAc})_6\text{Pyr}_{3,5}$  (20 mg,  $7 \times 10^{-3}$  mmol) were placed in a 125 ml conical flask and stirred at room temperature for 20 hours in air. Treatment of an aliquot of the reaction mixture according to procedure (a) and (β) (see below) afforded the oxidation products which were analysed by g.l.c.

(C') as in C except that  $\alpha$ -picolinic acid (4.9 g, 40 mmol) was used instead of trifluoroacetic acid.

#### Different Treatments of the Crude Aliquots were used throughout our Studies.

(α) To the aliquot (1 ml) in a test tube was added water (1 ml), ether (2 ml) and a solution of the internal standard in ether (1 ml). After cooling at  $-15^\circ\text{C}$  for 10–15 minutes, 50% (v/v)  $\text{H}_2\text{SO}_4$  (50 drops) was added, the test tube shaken and the mixture centrifuged. The supernatant was analysed by g.l.c.

(β) As in (α), except that the ethereal supernatant was decanted and transferred to another test tube containing acetone (1 ml). Ether was then removed from the test tube under reduced pressure. Three drops of the Jones reagent were added to the residual liquid (chiefly acetone = 1 ml) in the test tube. After stirring for 3 hours at room temperature under argon a saturated aqueous solution of sodium hydrogen carbonate (1.5 ml) was added dropwise to the stirred sample. Mild frothing ensued and after it had subsided, ether (2 ml) was added, the test tube shaken and centrifuged. The clear organic phase was analysed by g.l.c.

(γ) An aliquot (1 ml) of the reaction mixture was transferred to a test tube and treated directly with 3 drops of the Jones reagent as in (β) above. Identical work-up gave a supernatant which was analysed by g.l.c.

(δ) Water (30 ml) was added to the reaction mixture after electrolysis. The mixture was subsequently transferred to a separatory funnel and extracted with ether (4x20 ml). The combined ether extracts were transferred to a volumetric flask (100 ml) and the volume was adjusted to 100 ml by addition of ether. To 2 ml of this solution were added water (1 ml) and the internal standard in ether (1 ml). After cooling at  $-15^\circ\text{C}$  for 15 minutes, 50% (v/v)  $\text{H}_2\text{SO}_4$  (50 drops) was added, the test tube shaken carefully and the mixture centrifuged. The supernatant was analysed by g.l.c.

#### General Procedure for the Isolation of Pyridine Coupled Products.

Water (30 ml) was added to the reaction mixture which after cooling in ice was acidified with  $\text{H}_2\text{SO}_4$  (50%, v/v), transferred to a separatory funnel and the black liquid extracted with ether to remove the neutral oxidised products and starting material. The aqueous phase was carefully basified in an ice-cooled bath with concentrated NaOH. The basic aqueous phase was again extracted with ether (4x100 ml). The combined organic layers were dried ( $\text{MgSO}_4$ ), filtered and evaporated under water pump vacuum. Pyridine, which constituted the major part of the residue, was then removed under high vacuum ( $\sim 0.5$  mmHg) at room temperature. The dark brown residue was chromatographed (preparative layer chromatography, eluant: chloroform–acetone 5:1, v/v). Fractions thus obtained were compared by t.l.c. to 2,2',2,3',2,4',3,3' and 4,4'-bipyridines and to the authentic pyridine–hydrocarbon coupled products (when available). After isolation the <sup>1</sup>H n.m.r. spectra of the respective fractions were recorded and compared to those of the various bipyridines and pyridine–hydrocarbon coupled products.

In the case of 1-methylcyclopentane 11 as substrate (89 mmol) no fraction which contained the two prepared authentic products of coupling 21 and 22 could be found. In the oxidation of adamantane 34 under Gif<sup>IV</sup> conditions the coupled products 1-(4'-pyridyl)-adamantane 39, 1-(2'-pyridyl)-adamantane 38 and 1-(2'-pyridyl)-adamantan-4-one 47 were isolated.

Cyclohexane 1 and 3-ethylpentane 5 as substrates (50 mmol) gave less than  $10^{-2}$  mmol. of pyridine-hydrocarbon coupled products. Cis-decalin 24 (50 mmol) gave approximately  $1.5 \times 10^{-1}$  mmol. of pyridine-hydrocarbon coupled products, i.e. 5.6% of the total of oxygenated products (ketones and alcohols). Trans-decalin 29 (50 mmol) afforded  $7 \times 10^{-2}$  mmol. of pyridine-hydrocarbon coupled products which represent 3% of the total oxygenated products.

#### Auto-oxidation of trans and cis-decalin (29) and (24).

Cis-decalin 24 (2 ml, 12.96 mmol) and trans-decalin 29 (2 ml, 12.58 mmol) were respectively placed in two separate test tubes and oxygen was bubbled through each at 110°C for 20 hours. After cooling to room temperature the oxygen flow was stopped and trimethylphosphite (1 ml, 8.48 mmol) was added dropwise to each test tube. The solutions were then stirred for 2 hours at room temperature whereupon sodium hydroxide (20%, w/v, 5 ml) was cautiously added and stirring allowed to continue for two hours. The respective contents of the two test tubes were transferred to different separatory funnels and extracted with ether (3x20 ml). The combined ether layers from each extraction were respectively back-washed with water, separated, dried (MgSO<sub>4</sub>). An aliquot (1 ml) of each of the ethereal solutions was treated as in (8) (see above) and analysed for its tertiary alcohol content. Trans-decalin 29 gave trans-9-decalol 32 (0.182 mmol) and cis-9-decalol 27 (0.127 mmol), trans/cis 1.43. Cis-decalin 24 afforded 32 (2.314 mmol) and 27 (1.221 mmol), trans/cis 1.89.

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