Tetrahedron Letters,Vol.27,No.25,pp 2849-2852,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

SELECTIVE OXIDATION OF SATURATED HYDROCARBONS USING AN ELECTROCHEMICAL MODIFICATION OF THE GIF SYSTEM.

Gilbert Balavoine[a], Derek H.R. Barton[b], Jean Boivin[b], Aurore Gref[a],
Nubar Ozbalik[a,b] and Henriette Rivière[a].

[a] Institut de Chimie Moléculaire d'Orsay, UA 255, C.N.R.S.,
Université de Paris-Sud, 91405 Orsay, France.

[b] Institut de Chimie des Substances Naturelles, C.N.R.S.,
91190 Gif-sur-Yvette, France.

Abstract - The Gif system for selective hydrocarbon oxidation can be carried out replacing the zinc by a cathodic electrochemical reduction; the yields obtained and the selectivities observed are very similar.

The selective oxidation of saturated hydrocarbons remains a major problem of considerable current interest. The Gif system[1] (triplet oxygen, acetic acid, pyridine, zinc and an iron catalyst) shows a selectivity different from all preceding systems in that it oxidises saturated hydrocarbons mainly to ketones and gives minor amounts of aldehydes. Tertiary hydrogen is only substituted in exceptional cases. The yields of ketone obtained (20-30%) are higher than those normally seen in comparable model systems using triplet oxygen. We are glad to report that the zinc used as a reductant can be replaced by the cathode of an electrochemical process. Comparable yields of oxidation products can be obtained.

Careful examination by cyclic voltammetry (to be reported in detail in a full paper) of all the components of the Gif system in the presence of a tetraethylammonium salt as conducting electrolyte showed that -0.6 to -0.7 volts (versus the S.C.E.) was the best potential to use since it permits the (formally) 2 electron reduction of oxygen in pyridine-acetic acid without direct reduction of the pyridinium ion.

Preliminary electrochemical experiments showed that (i) the mercury electrode was the best working cathode, (ii) the acidity of the medium diminished as the electrolysis proceeded, (iii) acetic acid could be replaced by α-picolinic acid or by trifluoroacetic acid, (iv) that pyridinium salts e.g. the tetrafluoroborate could replace the supporting electrolyte and finally, (v) that trifluoroacetic acid itself protonated the pyridine well enough to remove the need for any sort of supporting electrolyte.

These observations led us to a simple electrochemical system in a separated compartment cell (Table 1) using pyridine-trifluoroacetic acid-oxygen and the iron catalyst.

Table 1

$$\begin{array}{lccccc} & (\underline{1}) + & (\underline{5})^{a} + & CF_3CO_2H^{b} & \xrightarrow{O_2 \text{ stream, } 20°C} & (\underline{2}) + (\underline{3}) + (\underline{4}) \\ \text{(mmol)} & (2) & (25\text{x}10^{-3}) & (2\text{ml}) & V_c = -0.5 \text{ to } -0.6 \text{ V/S.C.E.} & \\ & & & & i = 50\text{-}90 \text{ mA} & \\ & & & & \text{Pyridine (30 ml)} & \end{array}$$

Q^c (cb.)	(2) %	(3) %	(4) %	Total %	C^2/C^3	(1) recovered (%)	η^d
600	0.65	0.80	7.25	8.7	12.4	-	10.2
1000	0.85	1.0	9.10	10.95	11.9	-	7.7
1500	0.95	1.15	10.5	12.6	12.3	-	6.0
2000	1.0	1.35	12.15	14.5	13.5	74	5.15
2500	1.1	1.45	13.1	15.65	13.2	68	4.4
3000	1.0	1.5	13.5	16.00	15.0	62	3.8

a) (5) = $Fe_3O(OAc)_6Pyr_{3.5}$, see Reference 1.

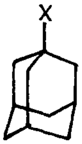
b) 3 ml of CF_3CO_2H were gradually added during the reaction to keep the "pH" in the region 4.5-5.5.

c) Aliquots were taken after the passage of the quantity of electricity indicated and were analyses by g.l.c.

d) The electronic yield η is based on the Cp450 equation $O_2 + 2e + 2H^{\oplus} \rightarrow H_2O + [O]$.

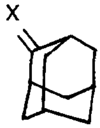
$$\eta = \frac{[4Nx + 2N\ (y + z)] \times 96.5}{Q_T}$$

where N = mmoles of substrate, x = % of (4), y = % of (2) and z = % of (3) (% based on substrate), Q_T = total electricity passed in Cb.[1 Faraday = 96,500 Cb.]



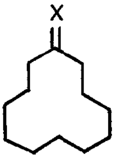
(1) X = H

(2) X = OH



(3) X = H, OH

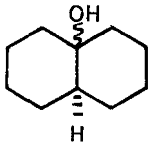
(4) X = O

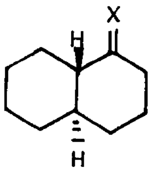


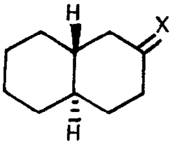
(6) X = H_2

(8) X = H, OH

(9) X = O


(10)


(7) $X = H_2$
(11) X = H, OH
(12) X = O


(13) X = H, OH
(14) X = O

The acidity of the medium was kept constant ("pH"4.5-5.5) by addition of further trifluoroacetic acid. Under these conditions the chemical yields and the selectivity of the normal Gif system could be equalled. C^2/C^3 is the total secondary products/tertiary products and is to be compared with the statistical number of 3. Analysis of the basic fraction for bipyridines (123 mg) and for pyridine-hydrocarbon coupled products (11% after 3,000 Cb.) gave very similar results to the chemical system.[1]

Comparable experiments were carried out on cyclododecane (6) and trans-decalin (7) with the results shown in the Table 2. In these experiments 1 mmol of 2,2'-dipyridyl was added at the beginning of the experiment. We consider that the iron is complexed with 2,2'-dipyridyl or with a reduced form of this compound during the oxidation process.

Table 2

$$\underset{\text{(mmol)}}{\text{(1) or (6) or (7)}} \;\underset{(2)}{}\; + \underset{(25\times10^{-3})}{5} + \underset{2\ \text{ml}^{a}}{CF_3CO_2H} + \underset{(1)}{\text{2,2'-dipyridyl}} \xrightarrow{O_2\ \text{stream, }20°C}$$

V_c = -0.7 V/S.C.E.
i^c= 80-100 mA
Q_T = 3000 Cb.
Pyridine (30 ml)

Substrate	Oxidation Products[b] %					Total %	C^2/C^{3c}	% Recovered Hydrocarbon	% Pyr.coupled Hydrocarbon	η
(1)	(2), 1.90	(3) (4) 16.1				18	8.5	65	10.5	4.2
(6)	(8), 1.4	(9) 19.7				21.1	-	60	1.0	5.2
(7)	(10) 0.6	(11) 0.9	(12) 9.0	(13) 0.65	(14) 11.0	22.2	36	50	1.4	5.4
(7)[d]	2.2	1.2	12.8	0.75	13.6	30.5	13	-	-	5.7

a) 3 ml. of CF_3CO_2H was added during the course of the oxidation to keep the pH close to 4.5. b) Analysed by g.l.c. and comparison with authentic samples.
c) The statistical numbers are as follows : (1) 3, (7) 8. d) Results obtained with the Gif Chemical system (pyridine-acetic acid - $Zn-O_2$-catalyst).

The ratio C^2/C^3 in the oxidation of adamantane has always played a major role in our discussion of the mechanism of oxidation.[1] A recent important paper[2] has shown that for radical attack by hydroxyl radicals a C^2/C^3 of 0.14 is seen. This is far from the number seen with the Gif system even when corrected for the formation of pyridine coupled (tertiary) products.

For the oxidation of trans-decalin reliable data for cobalt catalysed radical oxidation have recently become available[3] and show a C^2/C^3 of 0.13, far removed from the numbers 36 and 13 seen respectively in the electrochemical and chemical Gif systems.

In the chemical system the oxidant for the iron catalyst is not hydrogen peroxide.[1] We have made comparable experiments in the electrochemical system with the same results. We consider that the active form of reduced oxygen which *oxidises the iron catalyst is superoxide.*

Examination of the results reported in this preliminary Communication shows that the electrochemical system closely mimics the Gif chemical system in terms of efficiency and regioselectivity. We are convinced that further improvements are to be expected from simplification of the experimental technique and from more detailed mechanistic studies.

Acknowlegments : We thank B.P. (France) for generous financial support and Dr. D.J.H. Smith for helpful discussion.

References

1. D.H.R. Barton, M.J. Gastiger and W.B. Motherwell, J. Chem. Soc., Chem. Commun., 41 and 731 (1983); D.H.R. Barton, J. Boivin, N. Ozbalik and K. Schwartzentruber, Tetrahedron Lett., 41, 447 (1985) and references there cited; D.H.R. Barton, J. Boivin, M.J. Gastiger, J. Morzycki, R.S. Hay-Motherwell, W.B. Motherwell, N. Ozbalik and K.M. Schwartzentruber, J. Chem. Soc., Perkin I, in press; D.H.R. Barton, J. Boivin, W.B. Motherwell, N. Ozbalik, K.M. Schwartzentruber and K. Jankowski, J. Chem. Soc., Perkin I, submitted for publication.
2. J. Fossey, D. Lefort, M. Massoudi, J.-Y. Nedelec and J. Sorba, Can. J. Chem., 63, 678 (1985).
3. L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer and R. Weiss, J. Amer. Chem. Soc., 107, 3534 (1985).

(Received in France 28 April 1986)