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THE ELECTROCHEMICAL DIFUNCTIONALISATION OF SATURATED HYDROCARBONS

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The synthetic possibilities of the anodic oxidation of hydrocarbons have not been explored in any detail. Almost all investigations have been restricted to the region of the first anodic wave except for the case of readily oxidisable, polynuclear aromatics. Recently, we have shown for methyl benzenes[1] and adamantanes[2] that, in certain cases, both cation radical derived products and carbonium ion products can be obtained at the first wave thus demonstrating that the overall two electron process follows an e c e pathway. It was also shown for methyl benzenes that further anodic waves were accessible at higher potentials and that difunctionalisation could be accomplished in a single step at the second wave using acetonitrile as solvent.[3] The intermediate was shown to be either the dicarbonium ion or a carbonium/nitrilium ion. We now report the extension of anodic difunctionalisation to saturated hydrocarbons and in other media.

We have found that many hydrocarbons give more than one anodic wave in dry acetonitrile (AN) or in trifluoroacetic acid (TFA) using a suitable electrolyte. Table 1 lists the peak potentials obtained by linear sweep voltammetry for a number of saturated cyclic hydrocarbons, these values correlate well with the adiabatic ionisation potentials measured by photoelectron spectroscopy. Adamantane was chosen for detailed investigation. The two waves observed in acetonitrile were irreversible at all sweep speeds up to 10V s^{-1} and were of equal height, as was observed for hexamethylbenzene (HMB) and durene[3]. Preparative electrolysis at the first and second waves in acetonitrile gave the results of Table II after quenching with water. As was the case with HMB, high yields of monoamide and diamide were obtained at the first and second waves respectively and, at the higher potential, some monoamide was found, the amount depending upon the extent of the electrolysis. Diamantane also formed diamides at the second wave. Other workers[4] have reported two anodic waves, each of two electrons, for adamantane in acetonitrile. In that work, electrolysis was restricted to the region of the first wave and monoamide was isolated in high yield.

Preparative electrolyses were also performed in TFA to see if the pattern of monocarbonium ion and dicarbonium ion products could be observed in another medium. This is a considerably more acidic solvent and it allows access to a third wave in some cases, (Table I). Nyberg[5] has shown that HMB in TFA/CH_2Cl_2 could be oxidised to the disubstituted product at a higher potential after initial electrolysis at the first wave. Table II shows the result for adamantane for electrolysis at the first wave, electrolysis at the second wave, and for electrolysis at the second wave following an initial 2F $mole^{-1}$ electrolysis at the first wave. The pattern is similar to that observed in AN. It is interesting to note the appearance of monosubstituted product during the single step electrolysis at the second wave. This could be explained by a reproportionation reaction of the dicarbonium ion formed at the second wave as was postulated for HMB[3]. As was observed at the first wave, substitution at the second wave was almost exclusively at the bridgehead positions. This preference was confirmed by electrolysis of adamantan-2-ol (present at the trifluoroacetate ester) for which only secondary - tertiary products were observed.

The electrochemical data of Table I indicates that a wide range of hydrocarbons may show similar behaviour to that reported in detail for HMB and adamantane. There are, of course, several factors which will greatly influence the yields of product in other cases. These will include the stability of the carbonium ion towards elimination and the susceptibility of the substrate towards electrophilic attack by the carbonium ion. We believe, however, that this simple, single-step anodic route to disubstituted products has considerable synthetic potential.

References

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Table I

Voltammetric and Photoelectron Spectroscopy data for Various Hydrocarbons

Hydrocarbon	Peak Potential of First Wave (V)	Peak Potential of Second Wave (V)	Peak Potential of Third Wave (V)	Adiabatic I_p (eV)
Adamantane[a]	2.53	3.00		9.20
Adamantane[b]	1.91	2.38	2.83	
1,3-dimethyl adamantane	2.56	3.00		9.15
Diamantane[c]	2.37	2.68	3.08	8.59
cis and trans decalin (1:1)	2.80	3.25		∿9.35
Cyclohexane[b]	2.55	3.10		
Bicyclo(3,3,1) nonane	2.77	3.30		9.35

Peak potentials measured from linear sweep voltammograms at 0.3V s^{-1} for 10^{-2}M substrate in 0.1M $Bu_4^n NBF_4$ in acetonitrile. In each case the badkground currents are small.

[a] Similar peak potential and I_p's for ethyl, isopropyl, tert butyl, and trimethyl tertiary butyl adamantane.

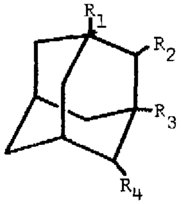
[b] $Bu_4^n NBF_4$ (0.1M) TFA-TFAn (1%) solution. Silver wire reference electrode.

[c] Saturated solution due to limited solubility.

Table II

Products and Yields from the Anodic Oxidation of Adamantane

Solvent	Potential of Oxidation (Volts)	Products and Yields
Dry Acetonitrile	2.5[a]	(i) 74% [c]
"	3.0[a]	(i) 6%, (ii) 58% [c,h]
Trifluoroacetatic acid + 1% Trifluoroacetic anhydride	1.8[b]	(iii) 83% [d]
"	2.3[b]	(iii) 12%, (iv) 2%, (v) 51% (vi) 5%[g], (vii) 1% [d]
"	1.8 then 2.3[b,e]	(iii) 4%, (v) 70% [d]
"	2.3 [b,f]	(vi) 44%, (vii) 11% [d]



(i) R_1 = $NHCOCH_3$; R_2, R_3, R_4 = H

(ii) R_1, R_3 = $NHCOCH_3$; R_2, R_4 = H

(iii) R_1 = OH; R_2, R_3, R_4 = H

(iv) R_2 = OH; R_1, R_3, R_4 = H

(v) R_1, R_3 = OH; R_2, R_4 = H

(vi) R_1, R_4 = OH; R_2, R_3 = H

(vii) R_1, R_2 = OH; R_3, R_4 = H

a. Reference electrode = Ag/Ag^+ (0.01M)
b. Reference electrode = Ag wire
c. Products after quenching with water; g.l.c. determination of yields.
d. Products after ether work-up and hydrolysis; g.l.c. determination of yields.
e. Two-step electrolysis; 2 Faradays at 1.8 then 2 Faradays at 2.3.
f. Substrate adamantan-2-trifluoroacetate instead of adamantane.
g. 2:1 mixture of epimers by n.m.r.
h. M.p. of isolated product at 226-227°C in agreement with the literature.