Electrochemical Oxidation of Allenic Hydrocarbons in Acetonitrile

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The anodic oxidation of a variety of alkyl-substituted allenes, terminal and internal ones, has been investigated in acetonitrile. All compounds studied were found to undergo $2e^-$ oxidation followed by nucleophilic attack by acetonitrile and water molecules, to form products containing at least two of the following functional groups, C=C, $NHCOCH_3$, C=O, and OH. The effect of various parameters (concentration, electrolyte, oxidation potential, temperature, and anode material) on the electro-oxidation of a model compound (nona-1,2-diene) has been studied and a general mechanistic scheme is presented and discussed.

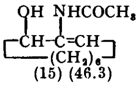
LITTLE is known about the anodic oxidation of allenic compounds. About two decades ago, Bockris and his co-workers[1] studied the oxidation of $CH_2=C=CH_2$ in basic aqueous media and reported that CO_2 was the sole product. Recently, we reported on the electrochemical oxidation of various alkyl-substituted allenes in methanol.[2] The reaction was found to be highly non-selective due to the formation of many products. Generally, both double bonds were oxidized to form α-methoxylated ketones, as well as esters due to exhaustive fragmentation. The reason for obtaining a high number of products is attributed to the formation of intermediate products containing electron-donating groups (methoxy) which were electroactive under the conditions studied and thus underwent further oxidation. Therefore, it is worthwhile looking into the electrochemistry of allenes in acetonitrile, anticipating a more selective process in this solvent.

RESULTS

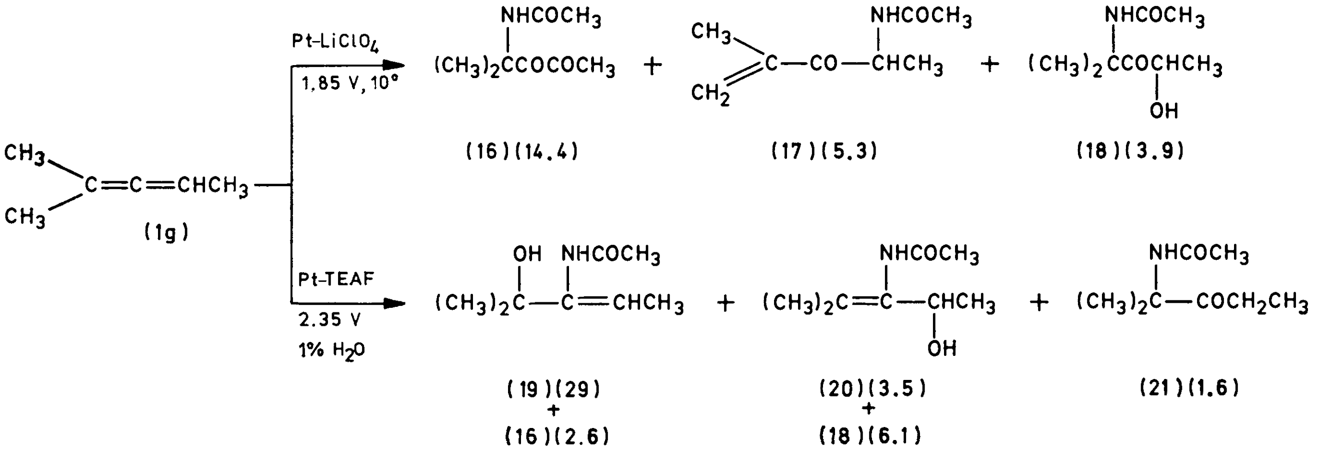
Various allenic hydrocarbons, nona-1,2-diene (1a), octa-1,2-diene (1b), hepta-1,2-diene (1c), 3-methylbuta-1,2-diene (1d), 3-methylpenta-1,2-diene (1e), cyclonona-1,2-diene (1f), and 2-methylpenta-2,3-diene (1g) were oxidised in acetonitrile at a Pt anode. Cyclic voltammograms of each of the compounds (1a—g) show a well defined first wave (in the region 1.7—1.9 V *versus* Ag–Ag$^+$) and an ill defined second wave in the region 2.0—2.3 V. In certain cases [*e.g.* (1c)] the two waves overlap each other and only a single one is observed (at 2.2 V). Controlled potential electrolyses for all substrates were carried out at *ca.* 2 V. Table 1 describes

TABLE 1

Products from electrochemical oxidation of allenic derivatives in CH_3CN–$LiClO_4$ on Pt anode, at ambient temperature [a]

Substrate	$R^1R^2C=C=CH_2$ R^1	R^2	Conc (mM)	Oxdiation potential(V)	$R^1R^2\overset{OH}{C}-\overset{NHCOCH_3}{C}=CH_2$	$R^1R^2\overset{NHCOCH_3}{C}COCH_3$	$R^1R^2\overset{OH}{C}COCH_3$	$R^1R^2C=\overset{NHCOCH_3}{C}CH_2OH$	$R^1R^2CHCOCH_2NHCOCH_3$	$R^1R^2C=\overset{NHCOCH_3}{C}CH_3$
(1a)	n-C_6H_{13}	H	77	1.95	(2) (35.4)	(3) (13)	(4) (5.8)			
(1b)	n-C_5H_{11}	H	74	1.9	(5) (40)	trace	trace			
(1c)	n-C_4H_9	H	74	2.1	(6) (22.5)	trace	trace			
(1d)	CH_3	CH_3	102.5	1.9	(7) (5.5)			(8) (19.8)		(9) (3.5)
(1d)			119	1.9 [b]	(7) (7.1)	(10) (3.7)		(8) (7.9)	(11) (3.7)	
(1d)			128	2.0			(12) (37.6) [c]			
(1e)	CH_3	C_2H_5	85.4	1.95		(13) (3.6)		(14) (5.8)		
(1f)	Cyclonona-1,2-diene		120	1.85	 (15) (46.3)					

[a] Figures in parentheses relate to chemical yields determined by g.l.c. [b] At 0 °C [c] At graphite, using 1% H_2O in CH_3CN–TEAF, only 28% of (12) was formed when (1d) was oxidized at 2 V.



SCHEME 1

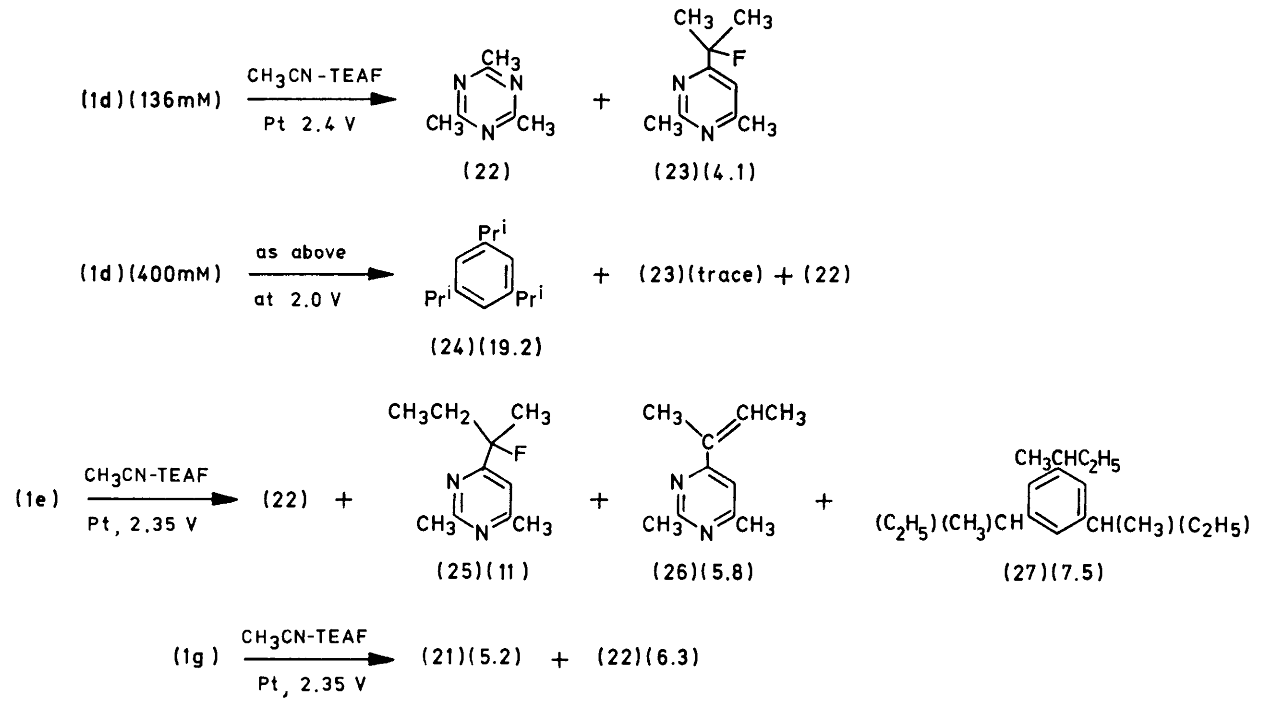


Table 2

Electrochemical oxidation of nona-1,2-diene (1a) in acetonitrile under various conditions

Experiment	Conc. (mM)	Oxidation potential(V)	Anode–electrolyte	n(F mol^{-1})	Yield (%)	Product yield (%) (2)	(3)	(4)	Unchanged (1a)	$Z^c = \frac{(2)}{(3)+(4)}$
1	36.6	1.4	Pt–$LiClO_4$	2.36	52	25.9	10.0	16.0	14.3	1.00
2	34.5	1.4	Pt–$LiClO_4$ + 10% H_2O	2.4	25	10.8	6.8	7.0	7.1	0.78
3	34.5	1.4	C–$LiClO_4$	2.21	68	34.2	7.4	26.3	4.8	1.01
4	37.5	1.4	Pt–TEAF[b]	2.24	51	7.4	19.5	23.8	8.2	0.17
5	178.0	1.4	Pt–$LiClO_4$	2.1	52	(products and yields are similar to experiment 1)				1.0
6	37.5	1.4[a]	Pt–$LiClO_4$	1.67	46	16.1	12.6	17.2	24.2	0.54
7	34.5	1.95	Pt–$LiClO_4$	2.4	54	35.4	13.0	5.8	6.3	1.88

[a] At 0 °C. All other experiments were carried out at ambient temperature. [b] Tetraethylammonium fluoroborate. [c] Yields ratio.

the results obtained from the anodic oxidation of (1a—f), in terms of products (2)—(15) and yields.

Compound (1g) is a trisubstituted allene and was found to produce results which do not always follow the general scheme for the mono- and di-substituted allenes. The reactions in Scheme 1, each under different experimental conditions, demonstrate the versatility of the process. Other substitutes *e.g.* (1d) and (1e) also exhibited sensitivity towards changes in experimental conditions. When CH_3CN was ' dry ' and tetraethylammonium fluoroborate (TEAF) was used as the base electrolyte, aromatic heterocyclic compounds were formed either due to trimerization of acetonitrile molecules to form 2,4,6-trimethyl-*s*-triazine (22), or due to cyclization between two solvent molecules and one molecule of substrate to give pyrimidine derivatives (23), (25), and (26). Acid-catalysed cyclisation of (1d and g) yielded aromatic products (24) and (27), respectively. Controlled experiments proved that the formation of these products is not due to electrochemical oxidation.

Compound (1a) was chosen as a model compound for studying the effects of various parameters on its electro-oxidation. Table 2 describes the results obtained on changing electrolyte, electrode material, potential, and concentration.

Spectral data of all isolated products are summarized in Table 3.

DISCUSSION

On comparing the results obtained from the anodic oxidation of allenic hydrocarbons in acetonitrile with those obtained in methanol,[2] we may conclude that in the former solvent the reaction is more selective, especially because no fragmentation takes place. This result may account for the electron-withdrawing nature of the acetamido-group which inhibits further oxidation. Indeed, all products shown in Table 1 are due to a 2F mol^{-1} oxidation process, indicating that only one of the two double bonds in the allene is oxidized. The products which contain a carbonyl group are in fact the keto-form of preformed enols. As one would expect, the internal double bond in terminal allenes would be favourably

TABLE 3

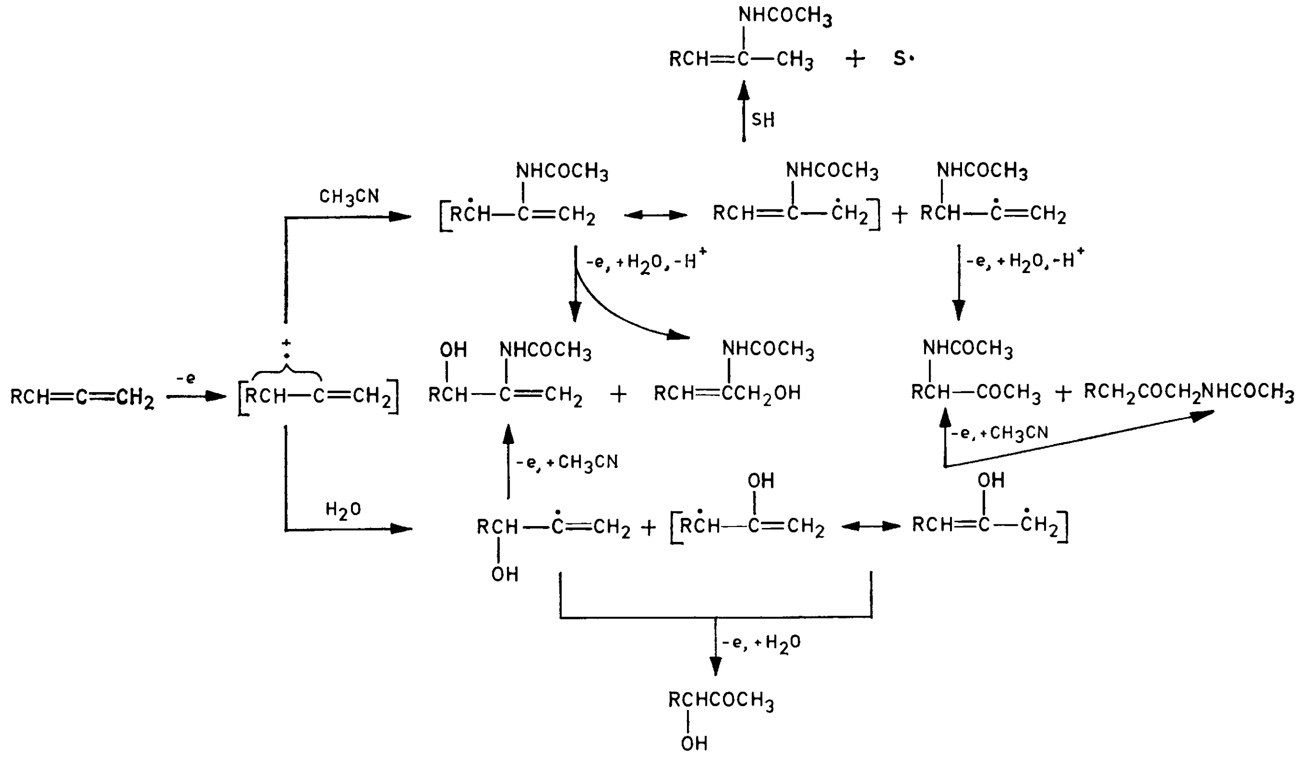
Spectral data of products isolated by g.l.c. after preparative electrolyses

Product	^{1}H Chemical shift δ (*J*/Hz)	I.r. (ν/cm^{-1}) [a]	M.s., *m/e* (%) [b]
(2)	0.86 (t, 3 H, *J* 6), 1.2—1.6 (m, 10 H), 1.96 (s, 3 H), 4.56 (q, 1 H, *J* 7), 5.17 (d, 1 H, *J* 2), 5.3 (d, 1 H, *J* 2)	3 280, 1 650, 1 530, 1 610	182 (M^+ – OH, 85), 132 (39), 114 (27), 90 (100), 60 (39), 43 (82)
(3)	0.87 (t, 3 H, *J* 6), 1.24—1.70 (m, 10 H), 2.0 (s, 3 H), 2.1 (s, 3 H), 4.62 (m, 1 H), 6.2 (1 H, br)	3 300, 1 720, 1 640, 1 530	199 (M^+, 22), 140 (23), 115 (31), 43 (100)
(4)	0.86 (t, 3 H, *J* 6), 1.24—1.72 (m, 10 H), 2.1 (s, 3 H), 4.9 (t, 1 H, *J* 8)	3 350, 1 730	148 (M^+, 21), 43 (100)
(5)	0.86 (t, 3 H, *J* 6), 1.2—1.8 (m, 8 H), 1.97 (s, 3 H), 4.57 (q, 1 H, *J* 7), 5.18 (d, 1 H, *J* 2), 5.3 (d, 1 H, *J* 2), 5.9 (d, 1 H, br)	3 300, 1 650, 1 530, 1 610	168 (M^+ – OH, 100), 132 (37), 90 (93), 60 (22), 43 (52)
(6)	0.9 (t, 3 H, *J* 6), 1.14—1.8 (m, 6 H), 1.97 (s, 3 H), 4.67 (q, 1 H, *J* 7), 5.20 (d, 1 H, *J* 2), 5.32 (d, 1 H, *J* 2), 6.42 (d, 1 H, br)	3 420, 1 670, 1 515, 1 620	171 (M^+), 154 (M^+ – OH, 83), 90 (100), 43 (43)
(7)	1.54 (s, 6 H), 1.92 (s, 3 H), 5.28 (d, 1 H, *J* 2), 5.33 (d, 1 H, *J* 2)	3 300, 1 660, 1 550, 1 630	126 (M^+ – OH, 100), 104 (48), 84 (42), 67 (100)
(8)	1.80 (s, 3 H), 1.84 (s, 3 H), 1.96 (s, 3 H), 4.06 (d, 2 H, *J* 5), 5.90 (1 H, br)	3 300, 1 660, 1 550, 1 630	126 (M^+ – OH, 100), 84 (52), 67 (29), 59 (33), 43 (36)
(9)	1.64 (s, 3 H), 1.7 (s, 3 H), 1.94 (s, 3 H), 3.8 (1 H, br)	3 350, 1 660, 1 515	127 (M^+, 14), 112 (15), 84 (85), 70 (100)
(10)	1.64 (s, 6 H), 1.94 (s, 3 H), 2.13 (s, 3 H), 3.8 (1 H, br)	3 350, 1 710, 1 660, 1 515	143 (M^+), 100 (15), 58 (100)
(11)	1.42 (d, 6 H, *J* 4), 2.01 (s, 3 H), 2.92 (m, 1 H), 4.26 (s, 2 H)	3 300, 1 720, 1 660, 1 530	143 (M^+, 2), 100 (100), 71 (63)
(12)	1.36 (s, 6 H), 2.09 (s, 3 H), 5.0 (1 H, br)	3 350, 1 720	102 (M^+, 39), 59 (30), 43 (100)
(13)	0.72 (t, 3 H, *J* 7), 1.5 (s, 3 H), 1.86 (q, 2 H, *J* 7), 1.96 (s, 3 H), 2.1 (s, 3 H)	3 400, 1 715, 1 650, 1 520	157 (M^+, 4), 114 (20), 86 (37), 72 (100), .43 (57)
(14)	0.84 (t, 3 H, *J* 7), 1.52 (s, 3 H), 1.85 (q, 2 H, *J* 7), 1.94 (s, 3 H), 5.4 (s, 2 H), 3.3 (1 H, br)	3 400, 1 650, 1 540, 1 620	140 (M^+ – OH, 10), 139 (36), 124 (100), 43 (25)
(15)	1.2—2.0 (m, 10 H), 1.96 (s, 3 H), 2.2 (m, 2 H), 4.5 (m, 1 H), 5.6 (t, 1 H, *J* 6)	3 320, 1 660, 1 520	180 (M^+ – OH, 100), 138 (19), 110 (69), 97 (40), 81 (24), 67 (31)
(16)	1.46 (s, 6 H), 1.88 (s, 3 H), 2.29 (s, 3 H)	3 400, 1 710, 1 650, 1 530	172 (M^+ + 1, 2), 128 (54), 101 (11), 100 (91), 86 (22), 43 (100)
(17)	1.32 (d, 3 H, *J* 7), 1.88 (s, 3 H), 1.96 (s, 3 H), 5.06 (m, 1 H), 5.84 (d, 1 H, *J* 2), 5 97 (d, 1 H, *J* 2)	3 300, 1 680, 1 650, 1 530	155 (M^+, 2), 86 (27), 69 (9), 44 (100)
(18)	1.44 (s, 6 H), 1.5 (d, 3 H, *J* 8), 2.08 (s, 3 H), 3.44 (s, 1 H), 5.60 (q, 1 H, *J* 8)	3 440, 1 725, 1 665, 1 540	173 (M^+, 2), 129 (6), 101 (51), 59 (25), 43 (100)
(19)	1.38 (s, 6 H), 1.8 (d, 3 H, *J* 6), 2.1 (s, 3 H), 4.6 (q, 1 H, *J* 6)	3 400, 1 660, 1 530, 1 625	157 (M^+), 140 (M^+ – OH, 5), 139 (41), 124 (100), 96 (15), 83 (25), 82 (28), 55 (14), 43 (27)
(20)	1.38 (d, 3 H, *J* 6), 1.65 (s, 3 H), 1.95 (s, 3 H), 2.05 (s, 3 H), 5.02 (q, 1 H, *J* 6)	3 400, 1 660, 1 530, 1 625	157 (M^+), 140 (M^+ – OH, 12), 139 (M^+ – H_2O, 59), 96 (77), 83 (88), 82 (29), 55 (41), 43 (100)
(21)	1.08 (t, 3 H, *J* 7.5), 1.46 (s, 3 H), 2.04 (s, 3 H), 2.48 (q, 2 H, *J* 7.5)	3 400, 1 715, 1 670, 1 550	157 (M^+), 156 (1), 101 (100), 57 (20), 55 (15), 42 (30)
(22)	2.57 (s, 9 H)	1 650	123 (M^+, 85), 82 (81), 42 (55), 40 (100)
(23)	1.63 (d, 6 H, *J* 22), 2.56 (s, 3 H), 2.62 (s, 3 H), 7.10 (s, 1 H)	1 660, 1 590	168 (M^+, 38), 167 (62), 153 (33), 147 (47), 122 (93), 67 (100), 42 (28)
(24)	1.25 (d, 18 H, *J* 7), 2.82 (m, 3 H, *J* 7), 6.79 (s, 3 H)		204 (M^+, 28), 189 (100), 161 (64), 105 (36), 91 (40), 43 (63)
(25)	0.79 (t, 3 H, *J* 7), 1.6 (d, 3 H, *J* 21), 1.96 (dq, 2 H, J_1 21, J_2 7), 2.49 (s, 3 H), 2.54 (s, 3 H), 7.1 (s, 1 H)	1 660, 1 595	183 (M^+ + 1), 167 (15), 154 (100), 153 (70), 122 (28)
(26)	1.86 (d, 3 H, *J* 6), 2.02 (s, 3 H), 2.44 (s, 3 H), 2.64 (s, 3 H), 6.68 (q, 1 H, *J* 6), 6.88 (s, 1 H)	1 640	162 (M^+, 46), 161 (59), 147 (100), 106 (23), 65 (79)
(27)	0.80 (t, 9 H, *J* 6), 1.24 (d, 9 H, *J* 6), 1.55 (m, 6 H), 2.54 (m, 3 H), 6.72 (s, 3 H)		246 (M^+, 10), 217 (100), 57 (38)

[a] Amides show two absorption bands in the regions 1 670—1 640 and 1 550—1 520 cm^{-1}, in addition to the NH stretching band at 3 300—3 400 cm^{-1}; C=C and C=N bonds give a weaker absorption in the region 1 630—1 590 cm^{-1}. [b] Major fragments only are reported. Chemical ionization or elemental analysis was employed for all products which failed to show a molecular ion peak, and satisfactory results were achieved in all cases.

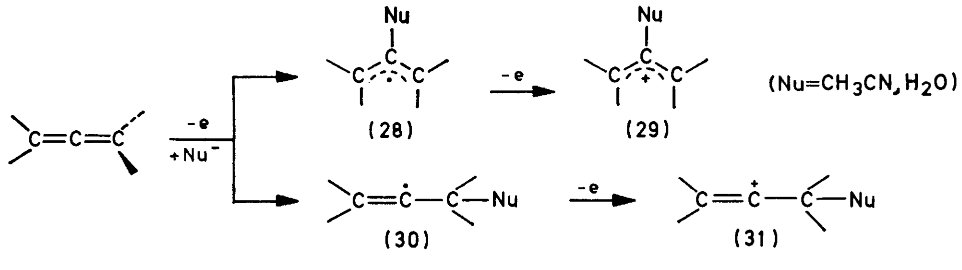
oxidized over the terminal one, due to the inductive effect exerted by alkyl group(s) attached to the former. Surprisingly, this was found to be the case only for the monoalkylated allenes (1a—c), whereas for (1d and e), the oxidation of the terminal double bond competes favourably with that of the internal one (see fourth and seventh entries in Table 1), in spite of the stronger inductive effect exerted by two alkyl groups. This phenomenon may be attributed to the steric effect exhibited by the two alkyl groups attached to one end of the allenic bond, forcing the other end to be closer to the electrode surface, and consequently to ozidize favourably. Such a phenomenon is also known in heterogeneous catalysis, *e.g.*, in the reduction of buta-1,2-diene on Pd, the formation of *cis*-but-2-ene was preferred over *trans*-but-2-ene although the latter is thermodynamically more stable. Moreover, no but-1-ene was observed and again, these results were explained by the steric effect of the methyl group causing the molecule to approach the catalyst surface from its other end.

In trimethylallene (1g), both double bonds are influenced by the inductive effect, and therefore, both are susceptible to oxidation. Indeed, this compound yielded products emerging from the anodic oxidation of both double bonds [*e.g.* (16)—(18)] as well as from either of them [*e.g.* (19) or (20)].



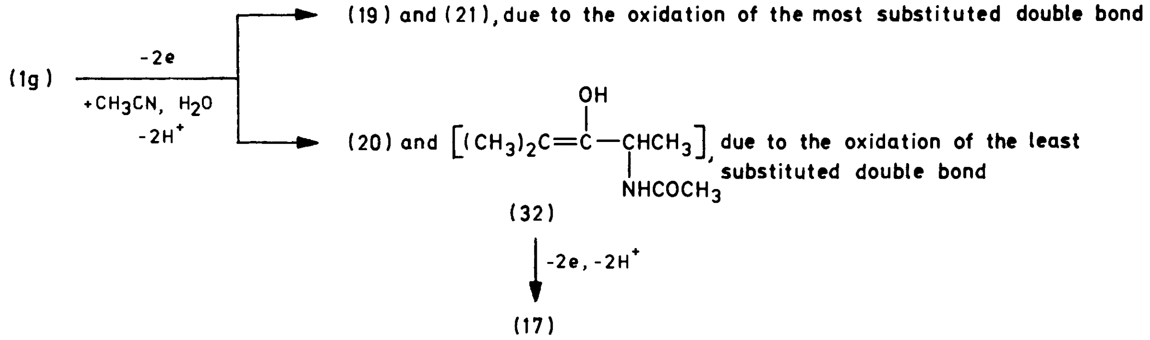
Scheme 2 A mechanistic pattern for the anodic oxidation of terminal allenes in acetonitrile

The low yield of products probably stems from the existence of several side reactions leading to the formation of oligomers or polymers. Radical intermediates or positively charged species may initiate chain reactions with an allenic substrate or with products containing activated double bonds, such as (17) and (26). Furthermore, acetamido-derivatives are known to undergo electrochemical polymerization.[4]



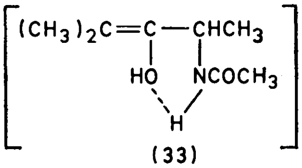
Both the nature of the products and the cyclic voltammograms support a mechanism which involves $2e^-$ oxidation and all the results obtained from the anodic oxidation of mono- and di-substituted allenes may be included in one mechanistic framework (Scheme 2). An initially formed cation-radical may react either with CH_3CN or with trace amounts of water (better nucleophile) to form radical intermediates which may undergo further oxidation and then react chemically to form the final products. It is noteworthy that no products due to dimerization or substitution at the α-position to the allenic bond were observed unlike the results reported for anodic oxidation of alkenes.[5,6]

As to the question at which carbon in an allene radical-cation the first nucleophilic attack takes place, our MO calculations[7] show that the central carbon is most susceptible to such an attack, regardless of the number of alkyl groups attached to the allene. Should that be the case, a stable allylic radical (28) or cation (29) may be formed. On the other hand, a nucleophilic attack on either end of the allene radical-cation leads to a vinyl radical (30) or cation (31) which are definitely less stable than (28) and (29), respectively. This hypothesis is also supported by the experimental fact that no diacetamido-derivatives were observed. Presumably a stable intermediate (29) is formed which is selective towards a second nucleophilic attack. Consequently, it reacts with water rather than acetonitrile, since the rate of the reaction with the former is faster by 5—6 orders of magnitude.



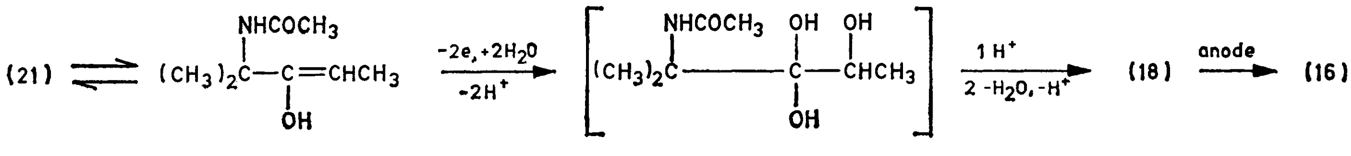
SCHEME 3

The mechanistic scheme does not explain the formation of some of the products obtained from (1g) since the latter undergo 4e$^-$ oxidation as well. The formation of (16)—(18) from 2e$^-$ oxidation product intermediates [*e.g.* (21) and (32)] may be rationalized by the pathways in Schemes 3 and 4. It is probable that due to the inductive effect of the two methyl groups, (32) undergoes slower 'ketonization' and the enol form* is immediately oxidized at the electrode surface to form (17). It cannot be excluded that the enol form is stabilized also by hydrogen bonding, such as in (33).



(33)

Similar arguments may hold for the formation of (18) and (16) from (21) (Scheme 4).



SCHEME 4

Table 2 describes a more thorough study on one of the allenic derivatives, (1a), which produces three major products (2)—(4) at different relative ratios, depending on the changed parameter. Consequently, the total yield could be increased to *ca.* 70% or reduced to *ca.* 25%. One product, (4), is totally due to reactions between reactive intermediates (formed electrochemically) and H_2O. Indeed, its relative amount increased in the presence of added water (compare experiment 2 with experiment 1), although the total yield decreases probably due to competitive oxidation of H_2O with the substrate. Changing the electrode material from Pt (experiment 1) to graphite (experiment 3) increases the total yield significantly. However, alteration of the electrolyte to TEAF (experiment 4) does not affect the total yield but changes the product ratio and (4) and (3) become favoured over (2). The most likely explanation of this behaviour is that the relative concentration of the nucleophiles at the electrode surface is not the same as in homogeneous solution and is strongly affected by the nature of the electrolyte. Nyberg proposed [9] that BF_4^- preferentially draws water into the double layer, thus discriminating against amide formation. Others suggested [10] that the cathodic process involving the reduction of the cation of the electrolyte, and which affects the acidity of the solution, plays an important role in the formation of the final products. To interpret our results, it is obvious that unlike product (2), in both (3) and (4) the central carbon is attacked by water rather than CH_3CN. Since the ratio Z = (2) : [(3) + (4)] is lowest in the presence of BF_4^- (exp. 4) one may follow Nyberg's suggestion [9] to explain the increased yield of (3) and (4) relative to (2). However, when ClO_4^- is the inert electrolyte, the weaker nucleophile CH_3CN is adsorbed favourably onto the electrode surface and thus the ratio Z increases, providing preferential formation of (2). A similar trend was found when $ArCH_3$ was oxidized in CH_3CN–ClO_4^-; $ArCH_2NHCOCH_3$ predominated over $ArCH_2OH$.[11]

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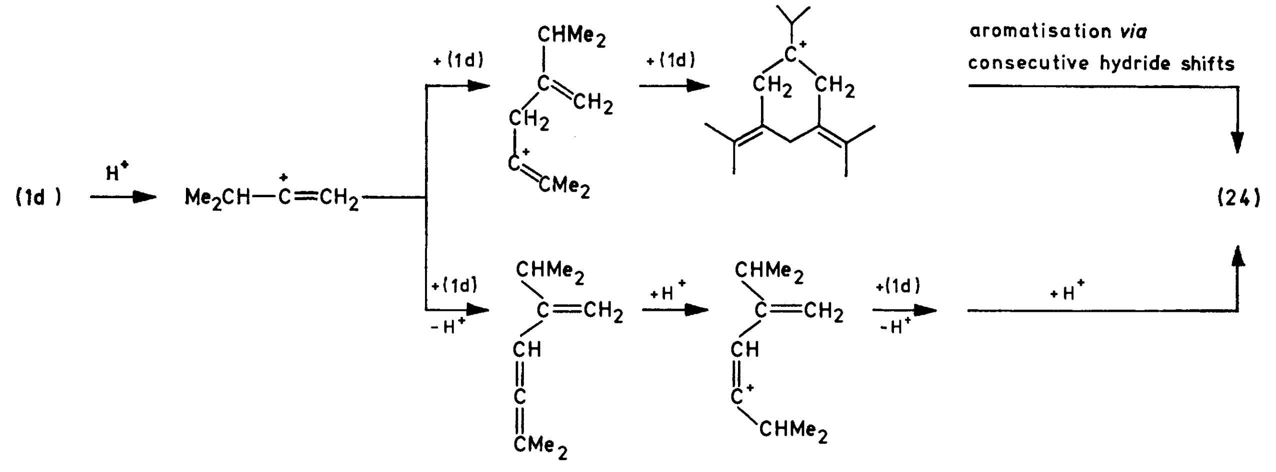
* It is known that the percentage of enol form is highly affected by inductive effects, *e.g.*, the proportion of enol form in $C_2H_5COCH_3$ is *ca.* 10^3 greater than in CH_3COCH_3.[8]

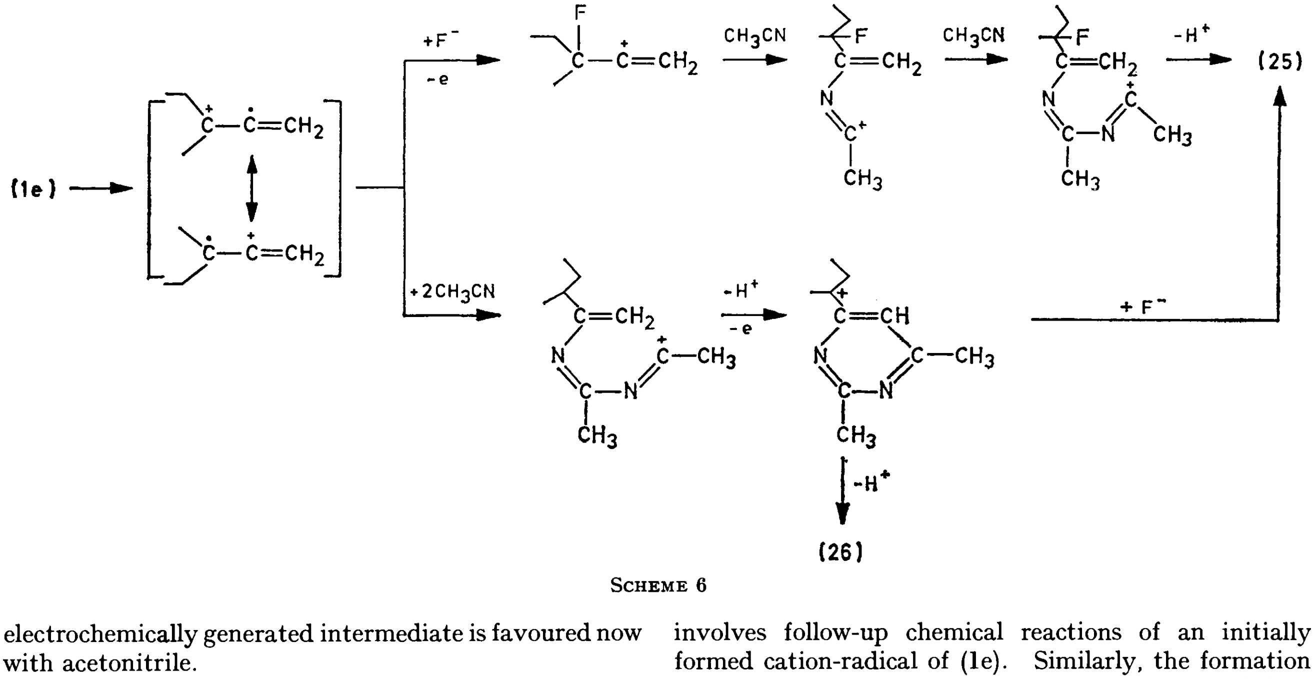
Upon increasing the concentration of (1a) by a factor of 5 (experiment 5 relative to 1) no measurable change was observed either in the total yield or in the product ratio. However, decreasing the reaction temperature (experiment 6) again resulted in a smaller value of *Z*. This result is quite reasonable since lowering the temperature has a stronger effect on the kinetics of the weaker (CH_3CN) nucleophile than those of the stronger one (H_2O). Finally, at a higher oxidation potential (experiment 7) the *Z* ratio increased again since now the availability of 'free' water molecules on the anode surface is diminished due to its electrochemical oxidation at this potential. Consequently, the chemical reaction of any electrochemically generated intermediate is favoured now with acetonitrile.

As was shown in the former section, at higher oxidation potentials (*ca.* 2.4 V) and in the presence of BF_4^- in 'dry' CH_3CN, cyclic trimerizations took place. Compound (22) is known to be formed by both acid and base catalysis,[12] as well as in the anodic oxidation of propene in acetonitrile (the cation-radical of propene was suggested to be the source of protons).[5] Similarly, the formation of (24) and (27) may also be explained by an acid-catalysed process (Scheme 5).



Scheme 5

An incorporation of a substrate molecule into the 'cyclic trimerization' process has a precedent in the literature[5] (formation of a pyrimidine derivative from two acetonitrile molecules and one molecule of propene) as well as fluorination (by BF_4^-) of benzaldehyde to form benzoyl fluoride.[13] To explain the formation of (25) and (26) we propose the mechanism in Scheme 6 which involves follow-up chemical reactions of an initially formed cation-radical of (1e). Similarly, the formation of (23) may be explained by both routes although it is difficult to test whether both, or only one, of them is applicable. We prefer the route which explains the



Scheme 6

formation of both (25) and (26), and is also consistent with our former hypothesis that initial nucleophilic attack is at the central carbon of an allene radical-cation.

EXPERIMENTAL

The syntheses or commercial source of the chemicals employed in this work, as well as electrochemical instrumentation, were described elsewhere.[2, 14] In a typical experiment octa-1,2-diene (1b) (243 mg, 2.2 mmol) was electrolysed in a three-compartment cell (H-type), employing a platinum gauze (2 × 2.5 cm) as the anode and Ag–$AgNO_3$ (0.1N) as the reference electrode. The concentration of (1b) in CH_3CN was 0.074M and 0.1M-$LiClO_4$ was used as supporting electrolyte. The mixture was potentiostatically oxidized at 1.9 V and electrolysis was terminated after passing 2.25 F mol^{-1} when the current reached its original background value (whenever the current decayed rapidly to low values a negative pulse to 0 V for 0.5 s was employed every 15—30 s). Then most of the solvent was evaporated (not to dryness!) and H_2O was added. The mixture was extracted three times into CH_2Cl_2, dried ($MgSO_4$), and filtered. The solvent was evaporated and the residue was injected into a g.l.c. column (SE-30 10% on Chromosorb W, $\frac{1}{4}$ in × 2 m) and products were collected for final analysis and characterisation (Table 3).

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