Tetrahedron Vol. 38, No. 11, pp. 1677 to 1682, 1982
Printed in Great Britain.

0040-4020/82/111677-06$03.00/0

ELECTROCHEMICAL OXIDATION OF ALKYL-SUBSTITUTED ALLENES IN METHANOL

JAMES Y. BECKER* and BARUCH ZINGER
Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel

(*Received in UK* 25 *September* 1981)

Abstract—Mono-, di- and tri-alkyl-substituted allenes were potentiostatically oxidized in methanol at graphite and Pt anodes. At the former electrode, α-methoxylated ketones (due to 4F/mole electricity consumption) and esters (6F/mole) were the major products. At a Pt anode, intermediate products such as vinyl-ether derivatives (2F/mole) were characterised too. Unlike the anodic oxidation of alkenes and alkynes previously reported in the literature, dimerisation is not a typical process in the allenes' oxidation, since of all the products obtained only a sole dimer has been observed. The mechanism for the formation of most products is discussed.

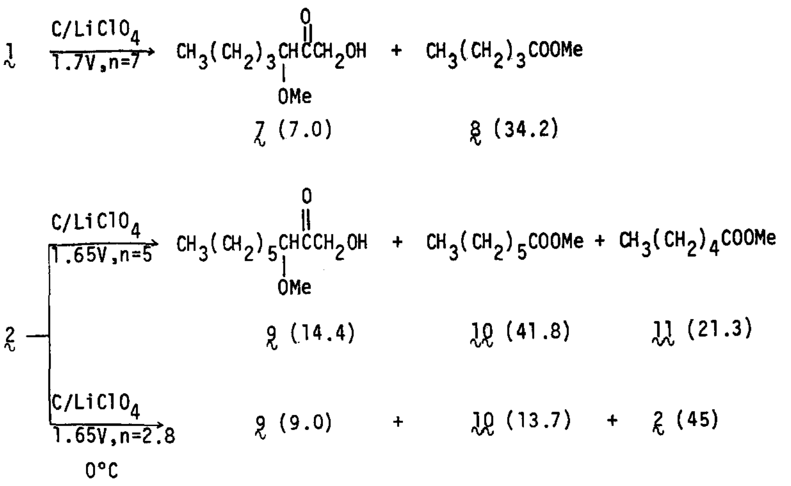
The electroreduction of allenic compounds in organic solvents as well as in the presence of proton donors has been studied by various research groups.[1-6] All of them used activated allenes in which the allenic bond is conjugated to 1–4 phenyl groups,[1,2] as well as to halogen,[2,3] alkoxy,[4] carbonyl[5] or sulfone[6] moieties. However, very little is known on the electrochemical oxidation of allenic derivatives. Allene itself was oxidized[7] in both acidic and basic aqueous media to yield CO_2. Recently we reported[8] on some preliminary results on the anodic oxidation of allenic hydrocarbons in methanol. In the present work we extend our study to a variety of alkyl substituted allenes, including one cyclic compound. The effects of electrode material, electrolyte, temperature and electricity consumption on the nature of products and their yield have been investigated.

RESULTS

The allenic derivatives, 1,2-heptadiene **1**, 1,2-nonadiene **2**, 3-methyl-1,2-butadiene **3**, 3-methyl-1,2-pentadiene **4**, 3-methyl-2,3-pentadiene **5** and 1,2-cyclononadiene **6** were anodically oxidized in methanol-L_iClO_4 at graphite (or some in methanol-MeO^-Na^+ at Pt).

$R^1R^2C{=}C{=}CR^3R^4$	R^1	R^2	R^3	R^4
1	n-C_4H_9	H	H	H
2	n-C_6H_{13}	H	H	H
3	Me	Me	H	H
4	Me	Et	H	H
5	Me	Me	Me	H
6	H	—$(CH_2)_6$—		H

The monosubstituted allenes, **1** and **2**, undergo $4e^-$ oxidation to yield ketone derivatives as well as $6e^-$ oxidation to form esters, as exhaustive products:



$$1 \xrightarrow[1.7V,n=7]{C/LiClO_4} \underset{\underset{7\ (7.0)}{}}{CH_3(CH_2)_3\underset{OMe}{CH}\overset{O}{\overset{\|}{C}}CH_2OH} + \underset{8\ (34.2)}{CH_3(CH_2)_3COOMe}$$

(1)†

$$2 \xrightarrow[1.65V,n=5]{C/LiClO_4} \underset{9\ (14.4)}{CH_3(CH_2)_5\underset{OMe}{CH}\overset{O}{\overset{\|}{C}}CH_2OH} + \underset{10\ (41.8)}{CH_3(CH_2)_5COOMe} + \underset{11\ (21.3)}{CH_3(CH_2)_4COOMe}$$

(2a)

$$2 \xrightarrow[1.65V,n=2.8\ \ 0°C]{C/LiClO_4} 9\ (9.0) + 10\ (13.7) + 2\ (45)$$

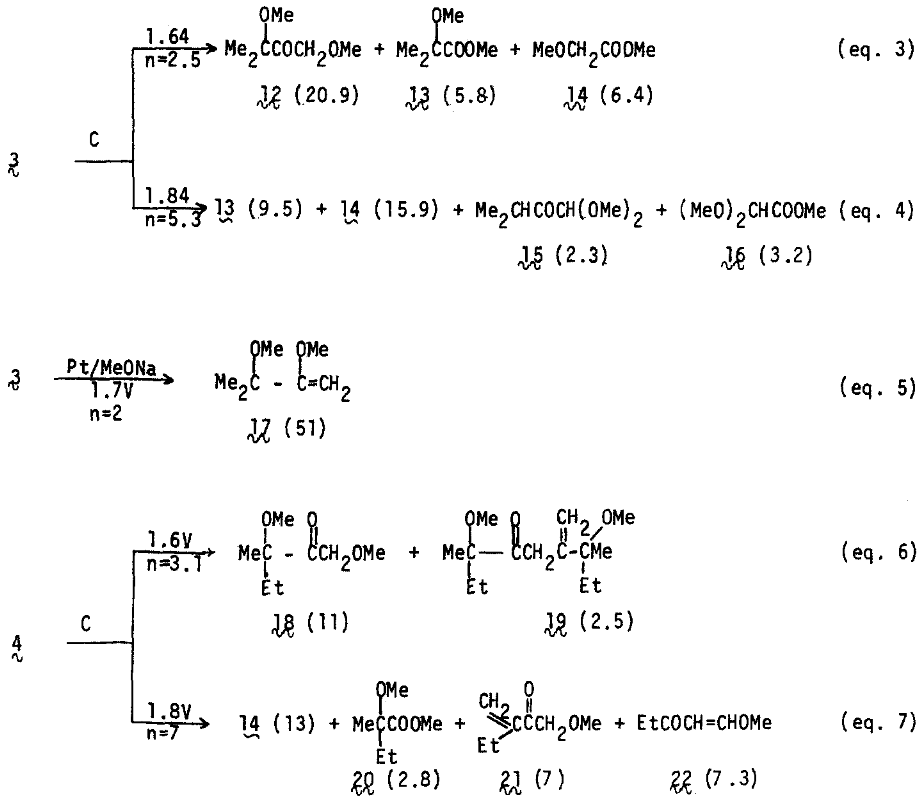
(2b)

Allenic derivatives with higher degree of substitution show less selectivity in terms of products and high sensitivity toward slight changes in the experimental

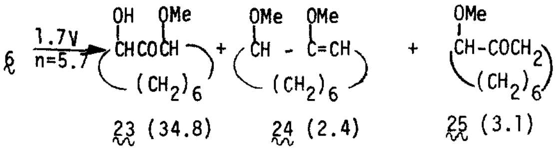
---

†The numbers in parentheses (throughout the article) correspond to chemical yield in %; n is the number of Faradays per mole of substrate.

conditions. Even compounds with the same number of alkyl groups, but slightly different (as in compounds **3** and **4**), do not behave as similarly as one would have anticipated. The following reaction equations demonstrate the "inhomogeneous" nature of substrates **3–6** towards the anodic process. (Each reaction yielded additional 5–8 products which occupied about 20–30% of the total area of all peaks in glc. These products are not shown in the reaction schemes since they have not been isolated or characterized.)



The cyclic compound **6**, undergoes mainly 2e⁻ and 4e⁻ oxidation processes. (The NMR of the crude mixture also shows a typical absorption of aldehyde presumably due to oxidative cleavage which results in ring-opening. However, this aldehyde could not be isolated.)



(eq. 8)

Trimethylallene **5** was investigated more thoroughly than the former ones. A typical example of what one gets

Table 1. Electrochemical data and products yield from the anodic oxidation of trimethylallene **5** at various conditions[a]

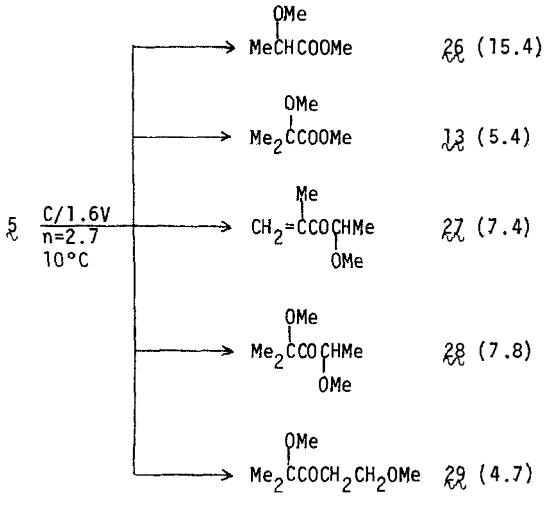
Experiment No.	Oxidation Potential (v)	anode/ electrolyte	n (F/mole)	cont. mM	total rcn. yield (%)	26	13	27	28	29
1	1.6	C/LiClO$_4$	2.7	102	40.7	15.4	5.4	7.4	7.8	4.7
2	1.6	"	5.4	102	41.3	24.2	5.3	4.4	6.3	1.1
3	1.6	"	10.9	102	54.5	43.8	10.7	-	-	-
4	1.6	"	2.5	59	45.9	28.3	11.6	4.2	0.9	0.9
5	1.7	Pt/LiClO$_4$	5.5	102	35.7	15.3	2.6	7.3	7.6	2.9
6	1.4	C/LiClO$_4$	4.0	102	82.5	50.1	10.2	9.3	7.9	5.0
7	1.7	Pt/MeONa	1.1	86	31.0	26.3	-	-	4.7	-

---

[a] All experiments were carried out at 10 ± 2°C. Potentials are cited vs. Ag/0.1N AgNO$_3$

Each experiment resulted in the formation of additional 5-8 unidentified products, with a total yield of 20 - 30%.

from its electrooxidation is shown below:

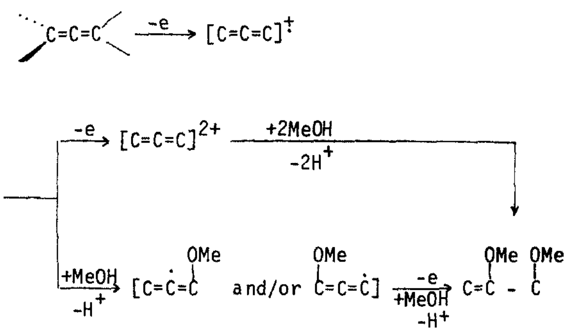


(eq. 9)

The effects of various parameters, such as electrode material, electrolyte, potential and others on the oxidation of **5** have been investigated and the results are summarised in Table 1.

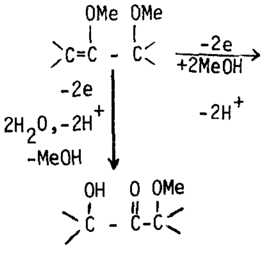
DISCUSSION

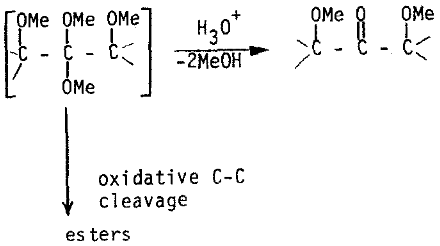
Both cyclic voltammetry and controlled potential experiments show a considerable increase in current upon addition of a substrate to the solvent-electrolyte mixture. This behaviour is a typical one for direct anodic oxidation of the depolarizer, along with similar observations found for oxidation of olefins[9] and acetylenes[10] in methanol. The wide spectrum of products obtained from the various allenes studied is due to $2e^-$, $4e^-$ and $6e^-$ oxidations. A substrate may undergo an ECEC (E-electrochemical, C-chemical steps) or an EEC mechanism, to explain the formation of the $2e^-$ oxidation products. An initially formed radical-cation may react with a solvent molecule and then be further oxidized followed by a second chemical step (ECEC). The other alternative consists of a further electrochemical oxidation of the cation-radical to form a dication which then reacts chemically with solvent molecules to produce the same product (EEC).



Such a mechanism was previously suggested for the oxidation of olefins in methanol.[11] Since an enol-ether contains a double bond activated by an electron-donating group, it has been found that on a graphite anode it oxidizes at a lower potential than its parent allene. This quality explains the observed increase of current throughout all electrolyses studied, despite the decrease in concentration of a substrate due to its consumption. Furthermore, it also explains the reason for not being able to isolate $2e^-$ oxidation products except in one case in which Pt-MeONa were employed with **3** (eqn 5). It turned out that the electrochemical oxidation of allenes at Pt takes place at higher potentials that at C by ~300 mV. On the latter anode, allenes and vinyl-ether intermediate products are strongly adsorbed at the surface allowing a more intimate interaction which facilitates further oxidation before diffusing away to the bulk solution. Apparently, when allenes were oxidized at Pt the initial current reached the background value after passing ~2F/mole, whereas at graphite the current did not fall to the background value and the reaction was terminated arbitrarily.

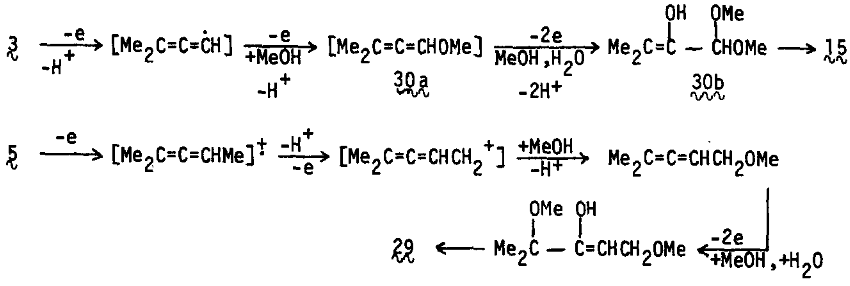
The electroactive vinyl-ether intermediates may undergo fast electrochemical reaction at graphite to form $4e^-$ oxidation products which in all cases were isolated





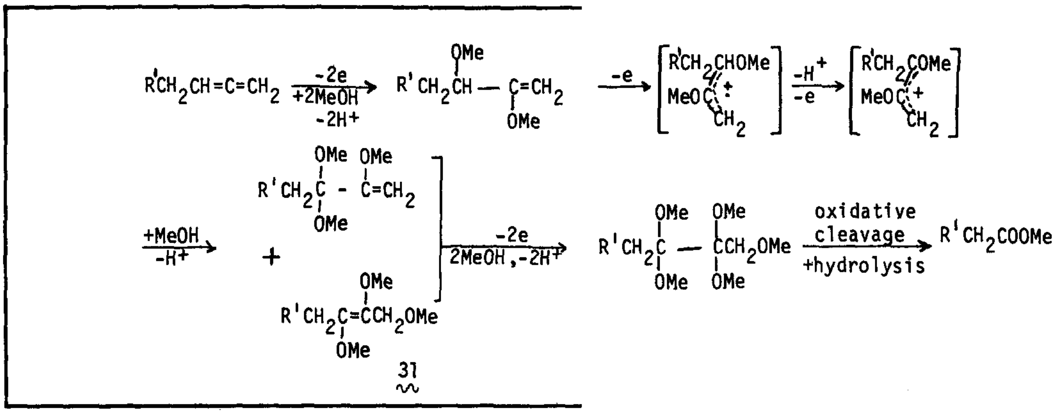
as ketones substituted with methoxy and hydroxy groups at the α-positions. Probably the pre-hydrolyzed tetramethoxylated intermediate cannot survive under the reaction conditions, and if not hydrolyzed it undergoes a $2e^-$ oxidative C–C bond breaking to produce ester derivatives. Similar anodic oxidative cleavage of activated C–C bonds was reported for phenylacetylene[12] and diols.[13]

So far, the above mechanistic schemes explain the formation of most of the products described in the former section, but not all of them. The formation of products such as **15**, (eqn 4) and **29** (eqn 9) needs a further rationalization which could be based on the assumption that the initially formed cation-radical loses a proton, either from a terminal allenic carbon or allylic position to produce **15** and **29**, respectively, as follows:



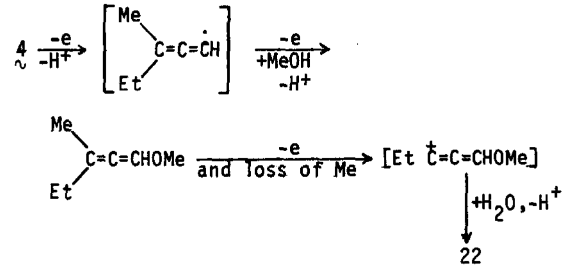
The loss of a proton from terminal allenic carbon is not surprising; allenic hydrogens are slightly acidic due to the electron-deficient nature of the bond. Moreover, they are expected to be even more acidic in the cation-radical species. A loss of a proton from the allylic position has precedents in the literature, in the case of anodic oxidation of propene and cyclohexene.[14]

Unlike the poly-substituted allenes which afforded α-methoxy esters as final products, the mono-substituted ones gave esters without any substitution at the α-position (eqns 1 and 2). More surprisingly, the oxidation of **2** resulted in the formation of two degraded esters, **10** and **11**. To explain these results one can describe at least one possible pathway, as follows:

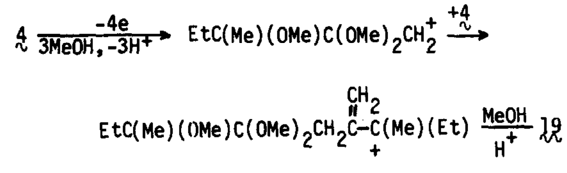


The intermediate product, **30a**, which contains an allenyl-ether bond, is susceptible to a facile anodic oxidation followed by tetra-methoxylation and C–C oxidative cleavage to yield **16** (eqn 4). The latter may also be formed by oxidative cleavate of **30b**, the enol form of **15**.

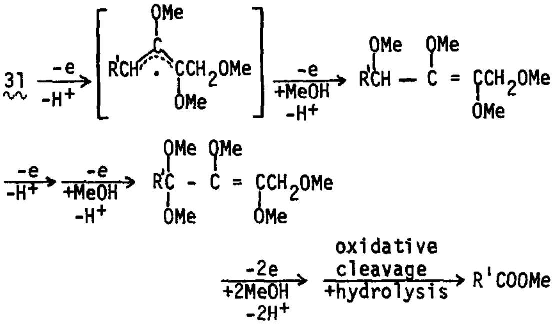
The formation of **22** (eqn 7) from **4** is quite unusual since it involves a loss of a methyl group. We suggest the following mechanism to rationalize its formation:



4 is the only allene which formed a dimeric product **19**. A possible mechanism for its formation may involve a reaction between cationic species and a molecule of **4**, as follows:



The production of **11** can be rationalized by assuming two further deprotonation steps following the oxidation of **31**:



On examining the effects of various parameters on the oxidation of **5** (Table 1) several conclusions may be reached:

(1) The higher the electricity consumption the more selective is the reaction in terms of products (entries 1–3). This trend is expected since the final exhaustive products are the esters, due to 6e$^-$/molecule oxidation. Indeed, the third entry shows that esters were the only two products formed.

(2) On changing the electrode material (compare entries 2 and 3 with 5) less fragmented products are formed on Pt than on C and the total reaction yield decreases on the former electrode. A possible explanation for this result is that polymerization is more

favourably catalysed on platinum than on graphite. Presumably the latter adsorbs *both* intermediates and solvent molecules, allowing them to react among themselves on its surface.

(3) On changing the electrolyte to a better nucleophile (compare entry 7 with 5) while the total yield remains basically the same, the reaction becomes more selective since only two products were detected in the presence of CH_3O^-.

(4) Entries 1 and 4 demonstrate the changes observed by varying the concentration. As expected, the higher the concentration the less exhaustive products (esters) were observed. At a higher concentration both substrate molecules and electroactive species competes towards the anodic process, whereas at a lower substrate concentration the electroactive intermediates have a better chance to undergo further oxidation and to produce esters.

(5) Entry 6 shows that, upon reducing the potential by only 200 mV, a tremendous increase in the total yield is achieved, although the number of products remains unchanged. Obviously, the low potential eliminates or decreases the further oxidation of electroactive intermediates to form by-products or oligomers.

(6) It is noteworthy that the favoured ester in all experiments is the one formed by cleavage of the most highly alkylated C–C bond, as is to be expected due to the inductive effect exerted by the alkyl groups.

CONCLUSION

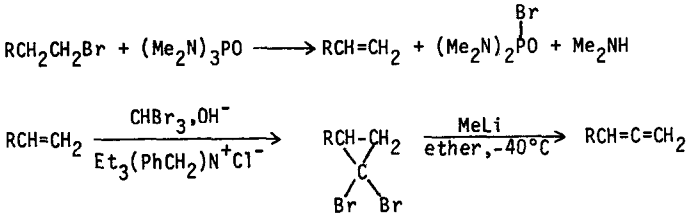
The allenic derivatives studied undergo oxidation to form vinyl-ethers, α-methoxylated ketones and esters. They are found to be highly sensitive to small structural changes within the molecule presumably due to both steric and inductive effects. This behaviour may account for their failure to obey a one mechanistic scheme. It is noteworthy that unlike alkenes and acetylenic compounds, they do not, in general, produce dimers.

For further studies on the electrochemical oxidation of allenic compounds as well as hetero-cumulenes, both in acetonitrile, see ref. 19.

EXPERIMENTAL

Materials and instrumentations. Spectrograde methanol, was distilled over Na and stored over molecular sieves. Before each experiment the solvent was passed through neutral and activated (heated for 5 hr at 150° in vacuum) alumina column. Allenes **3**, **4** and **5** were purchased from Aldrich and the others were prepared in our laboratory. A description of the electrochemical instrumentation, cyclic voltammetry and procedures for preparative electrolyses was published elsewhere.[15]

Preparation of **1**,*2-heptadiene* **1** *and* **1**,*2-nonadiene* **2**. Both materials were prepared from primary alkyl bromides according to the following reactions:



Preparation of 1-alkenes from their corresponding alkyl bromide was carried out according to a procedure in Ref. 16. Synthesis of 1,1-dibromocyclopropyl derivatives was carried out according to Ref. 17, followed by reduction with methyllithium to give the desired allenic derivatives.[18] In a typical example, 50 ml of 50% NaOH (by weight) was added dropwise to a mechanically stirred solution of 0.1 mole $CHBr_3$ (Fluka), 0.1 mole 1-hexene and 0.4 g triethylbenzylammonium chloride (TEBA), within 10 min at 40–50°C. Then the solution was left stirring for 3 hr at this temp (CH_2Cl_2 was added if the slurry was too thick). The mixture was added to 150 ml water and extracted into CH_2Cl_2. The organic phase was washed with 10% HCl, water, and dried over anhydrous $MgSO_4$. TEBA was prepared by refluxing equimolar amounts of Et_3N and benzyl chloride in dry benzene until a precipitate was formed. After filtration, the solid was dried overnight at 25 mmHg. The yield of the 1,1-dibromocyclopropyl derivatives was ~60%.

0.1 Mole of the 1,1-dibromocyclopropane derivative was diluted with 25 ml dry ether and cooled to −40°. 0.12 Mole of MeLi in ether was added dropwise within 30 min. The mixture was stirred for another 30 min at low temperature and then allowed to warm to ambient temp. Water was added slowly and the two phases were separated. The ethereal one was washed with water (until neutral to pH paper) and dried over $MgSO_4$. (MeLi was prepared from Li metal and MeBr in dry ether and titrated with a standard HCl soln.) The yields for compound **1** and **2** were 56 and 60%, respectively, after column chromatography on neutral alumina with n-hexane as eluent.

Preparation of 1,2-*cyclononadiene* **6**. This compound was made from commercial *cis*-cyclo-octene (according to a procedure cited in Ref. 18) and obtained in 81% yield.

Spectral data of products obtained from electrosynthesis (*mass spectra*, m/e *for molecular ion*; *IR*(cm^{-1}); ^{1}*H-NMR*, *δppm*, J_{Hz}). From oxidation of **1** at 1.75 V: **7** [160(M^+); 3300–3500, 1725; 0.9 (t, 3H, J = 6), 1.21 (m, 4H)), 1.6 (m, 2H), 3.24 (s, 3H). 3.6 (t, 1H, J = 6), 5.3 (s, 2H)]; **8** [116(M^+); 1740; 0.85 (t, 3H, J = 6), 1.45 (m, 4H), 2.26 (t, 2H, J = 6), 3.58 (s, 3H)].

From oxidation of **2** at 1.65 V: **9** [188(M^+); 3300–3500, 1730; 0.9 (t, 3H, J = 6), 1.21 (m, 8H)), 1.6 (m, 2H), 3.24 (s, 3H). 3.6 (t, 1H, J = 6), 5.3 (s, 2H)]; **10** [144(M^+); 1740; 0.86 (t, 3H, J = 6), 1.45 (m, 8H), 2.26 (t, 2H, J = 6), 3.58 (s, 3H); **11** [130(M^+); 1740; 0.86 (t, 3H, J = 6), 1.47 (m, 6H), 2.25 (t, 2H, J = 7), 3.57 (s, 3H)].

From oxidation of **3** at 1.6 V: **12** [146(M^+); 1730; 1.32 (s, 6H), 3.12 (s, 3H), 3.38 (s, 3H), 4.38 (s, 2H)]; **13** [132(M^+); 1740; 1.38 (s, 6H), 3.20 (s, 3H), 3.66 (s, 3H))]; **14** [104(M^+); 1740; 3.42 (s, 3H), 3.70 (s, 3H), 4.02 (s, 2H)].

Additional two products were formed from **3** at 1.8 V: **15** [146(M^+); 1725; 1.07 (d, 6H, J = 7), 2.97 (heptet, 1H, J = 7), 3.38 (s, 6H), 4.52 (s, 1H)]; **16** [134(M^+); 1740; 3.36 (s, 6H), 3.74 (s, 3H), 4.75 (s, 1H)].

From oxidation of **3** at Pt/MeONa: **17** [130(M^+); 1615; 1.32 (s, 6H), 3.12 (s, 3H), 3.52 (s, 3H), 4.03 (d, 1H, J = 2), 4.15 (d, 1H, J = 2)].

From oxidation of **4** at 1.6 V: **18** [160(M^+); 1720; 0.8 (t, 3H, J = 7), 1.24 (s, 3H), 1.72 (q, 2H, J = 7), 3.18 (s, 3H), 3.36 (s, 3H), 4.32 (s, 2H)]; **19** [0.86 (t, 3H), 0.90 (t, 3H), 1.34 (s, 3H), 1.38 (s, 3H), 1.72 (m, 4H), 3.14 (s, 3H), 3.22 (s, 3H), 3.68 (s, 2H), 5.3 (d, 1H), 5.34 (d, 1H)], and at 1.8 V: **20** [1745; 0.96 (t, 3H, J = 7), 1.56 (s, 3H), 1.68 (q, 2H, J = 7), 3.2 (s, 3H), 3.74 (s, 3H)]; **21** [128 (M^+); 1685, 1615; 1.05 (t, 3H, J = 8), 2.32 (q, 2H, J_1 = 8, J_2 = 1.5); 3.39 (s, 3H), 4.37 (s, 2H), 5.65 (t, 1H, J = 1.5), 5.84 (s, 1H)]; **22** [114 (M^+); 1680, 1620; 1.06 (t, 3H, J = 8), 2.34 (q, 2H, J = 8), 3.68 (s, 3H), 5.45 (d, 1H, J = 2), 6.04 (d, 1H, J = 2)].

From oxidation of **5** at 1.6 V: **26** [118 (M^+); 1745; 1.35 (d, 3H, J = 7), 3.32 (s, 3H), 3.68 (s, 3H), 3.74 (q, 1H, J = 7)]; **27** [1680, 1625; 1.36 (d, 3H, J = 7), 1.9 (s, 3H), 3.28 (s, 3H), 4.38 (q, 1H, J = 7); 5.78 (s, 1H), 6.04 (s, 1H)]; **28** [1715; 1.28 (d, 3H, J = 7), 1.3

(s, 6H), 3.22 (s, 6H), 4.42 (q, 1H, J = 7)] **29** [1710; 1.24 (s, 6H), 2.80 (t, 2H, J = 6), 3.16 (s, 3H), 3.26 (s, 3H), 3.60 (t, 2H, J = 6.

From oxidation of **6** at 1.7 V: **23** [186 (M^+); 3400–3600, 1715; 1.34–2.1 (m, 12H), 3.32 (s, 3H), 3.62 (t, 1H, J = 8), 4.0 (t, 1H, J = 6)]; **24** [1.2–2.0 (m, 8H), 2.0–2.3 (m, 4H), 3.28 (s, 3H), 3.68 (s, 3H), 4.0 (m, 1H), 6.1 (m, 1H)]. Both **24** and **25** were obtained with impurities.

REFERENCES

[1] R. Dietz, M. E. Peover and R. Wilson, *J. Chem. Soc.* (*B*) 75 (1962); R. Dietz and E. Larcombe, *Ibid.* 1369 (1970); A. E. J. Forno, *Chem. Ind.* (*London*) 1728 (1968); A. Zweing and A. K. Hoffman, *J. Am. Chem. Soc.* **84**, 3278 (1962); W. M. Moore and D. G. Peters, *Ibid.* **97**, 139 (1975).

[2] H. Doupeux, P. Martinet and J. Simonet, *Bull. Soc. Chim. Fr.* 2299 (1971).

[3] J. Simonet, H. Doupex, P. Martinet and D. Bretelle, *Ibid.* 3930 (1970); J. Simonet, H. Doupeux and D. Bretelle, *C. R. Acad. Sci., Paris, Ser. C.* **270**, 59 (1970).

[4] E. Santiago and J. Simonet, *Electrochim. Acta* **20**, 853 (1975).

[5] P. Martinet, J. Simonet and M. Morenas, *Bull. Soc. Chim. Fr.* 814 (1970).

[6] R. W. Howsam and C. J. M. Stirling, *J. Chem. Soc. Perkin II* 847 (1972).

[7] J. O'M. Bockris, H. Wroblowa, E. Gileadi and B. J. Piersma, *Trans. Farad. Soc.* **61**, 2531 (1965); H. Wroblowa, B. J. Piersma and J. O'M. Bockris, *J. Electroanal. Chem.* **6**, 401 (1963); *J. Electrochem. Soc.* **111**, 863 (1964).

[8] B. Zinger and J. Y. Becker, *Electrochim. Acta* **25**, 791 (1980).

[9] N. L. Weinberg and H. R. Weinberg, *Chem. Rev.* **68**, 449 (1968); S. D. Ross, M. Finkelstein and E. J. Rudd, in *Anodic Oxidations*, pp. 112–113. Academic Press, New York (1975).

[10] M. Katz and H. Wendt, *J. Electronal. Chem.* **53**, 465 (1974).

[11] M. Katz, P. Riememschneider and H. Wendt, *Electrochim. Acta* **17**, 1595 (1972).

[12] M. Katz, O. Saygim and H. Wendt, *Ibid.* **19**, 1973 (1974).

[13] T. Shono, Y. Mutsumura, H. Hashimoto, K. Hibina, H. Hamaguchi and T. Aoki, *J. Am. Chem. Soc.* 2546 (1975).

[14] T. Kanbe and T. Fueno, *J. Org. Chem.* **42**, 2313 (1977); D. Clark, M. Fleischmann and D. Pletcher, *J. Electroanal. Chem.* **36**, 137 (1972); T. Shono and I. Ikeda, *J. Am. Chem. Soc.* **94**, 7892 (1972).

[15] J. Y. Becker and D. Zemach, *J. Chem. Soc. Perkin II* 914 (1979).

[16] R. S. Monson, *J. Chem. Soc. Chem. Comm.* 113 (1971).

[17] M. Makaska and M. Fedorgnski, *Syn. Comm.* **3**, 305 (1973).

[18] L. Skatteböl, *Acta Chem. Scand.* **17**, 1683 (1963).

[19] J. Y. Becker and B. Zinger, *J. Chem. Soc. Perkin II*, in press; *J. Amer. Chem. Soc.* in press.