

most exclusively trans products (with only trace amounts of cis products). In accordance with solvolytic results,^{2c} the 7-perhydropentalenyl cation gave only olefins, owing to the instability of the trans products. In no case, under the reaction conditions used, did isomerization between the cis and trans products take place.

Experimental Section

Preparation of the bridgehead cations was carried out as previously described.⁴⁻⁶

Quenching of solutions of bridgehead cations was carried out in either MeOH-NaOMe or NaBH₄-SO₂ClF by the previously described procedure.⁵ Products were extracted with carbon tetrachloride and the combined extracts were washed, dried (MgSO₄), concentrated, and then analyzed by glc using comparison with authentic samples.^{2c} Data of parallel experiments are summarized in Table I.

Carbon-13 nuclear magnetic resonance spectra were obtained using a Varian Associates Model XL 100 nmr spectrometer equipped with a Fourier transform accessory, a spin decoupler, and a variable-temperature probe. The pulse width used was 15-20 μsec, and the need to provide multichannel excitation over the range of interest (10,000 Hz) limited the data acquisition time to 0.4 sec. Approximately 500-1000 accumulations were made for satisfactory spectra, depending on the ion concentration. A Varian 620L computer was used to accumulate data. The external lock used was fluorobenzene. Fourier transformation of the accumulated free induction signal gave the frequency spectrum, from which was obtained the chemical shift of each signal relative to the external signal of a 5% ¹³C enriched TMS capillary. Coupling constants (in hertz) were directly obtained from the coupled cmr spectra. However, in these cases longer accumulation times were required. Pulse delay and pulse width used were 0.5 sec and 35 μsec, respectively.

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Registry No. 1, 23373-80-0; 2, 29921-17-3; 3, 28358-57-8.

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Remote Anodic Acetamidation of Esters via Carbonium Ions

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The anodic oxidation of several acyclic esters has been performed in acetonitrile solution. A platinum anode, a divided cell, and potentiostat were employed. When lithium perchlorate was the electrolyte, a very clean conversion of ester to monoacetamidated ester took place. Ethyl butanoate, for example, produced ethyl 3-acetamidobutanoate in 70% yields when 3 faradays/mol of electricity was passed. Selectivity for ω-1 substitution was also found with other substrates. Although tetraethylammonium fluoroborate as electrolyte provides the same product it is shown that electrolyte oxidation processes are intimately involved in this acetamidation process. Thus, it is required that the potential be high enough [LiClO₄, 2.74, and (CH₃CH₂)₄NBF₄, 3.10] to oxidize the electrolyte in order to get good yields of product. The intermediacy of a carbonium ion is proposed to explain the formation of acetamides and the formation of rearranged products from the oxidation of methyl pivalate.

This study commenced as a survey of the anodic chemistry of aliphatic compounds. Our primary goal was to establish the common reactions of simple molecules.² Additionally, we hoped that the energetic intermediates generated at high potentials would lead to unique and useful reactions. We report here on the anodic products from esters in acetonitrile solvent. Although the reaction conditions (other than potential) are very mild, this process generates aliphatic carbonium ions from ordinary alkyl groups. It also provides a method for acetamidation at remote positions, a reaction which cannot be directly accomplished by other means.

Anodic substitution of acetamide for an activated (allylic, benzylic) hydrogen is well documented.³ Of particular importance to this study is the extension of this reaction to certain saturated hydrocarbons. The oxidation of

adamantane in acetonitrile-lithium perchlorate, for example, produces 1-adamantylacetamide in 90% yield.² The oxidation of octane in acetonitrile-tetraethylammonium fluoroborate gives an equal mixture of 2-, 3- and 4-octyl acetamides in 40% yield.⁴ In contrast to the esters studied here each of these hydrocarbons oxidizes at a potential below that which is necessary for oxidation of the electrolyte.

Results

Oxidations were performed potentiostatically in a three-compartment cell at a platinum anode. The reference electrode was a silver wire immersed in 0.1 M AgNO₃ in acetonitrile. The anolyte and catholyte were acetonitrile-0.1 M lithium perchlorate. Background current without added substrate varied in individual experiments from 120

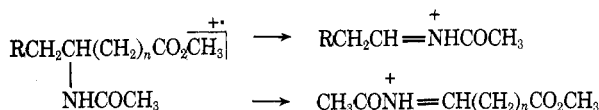
Table I
Current-Concentration Data for Ethyl Butyrate^a

Concn, $M \times 10^3$	i , mA	Concn, $M \times 10^3$	i , mA
0	155	21.0	200
4.2	180	25.2	200
8.4	190	29.4	200
12.6	195	33.6	200
16.8	195		

^a Data taken under the usual preparative conditions at 2.74 V vs. Ag/AgNO₃.

to 250 mA at 2.75 V. Addition of substrate raised this value about 15%. This current was largely independent of which ester was added, and the value was independent of the ester concentration above 0.04 M (Table I). In a typical run, 3 mmol of ester was oxidized over a 3-hr period. The current did not change with time. Oxidations were discontinued after 2-4 faradays/mol was passed. Each reaction was worked up by careful evaporation of much of the acetonitrile, neutralization with aqueous base, and extraction with chloroform. The chloroform layer generally contained *only* the monoacetamidated products reported in Table II.

The amide products were generally purified chromatographically and identified spectroscopically. The mass spectra of these and other amides⁵ all showed intense peaks corresponding to the following processes.⁶



Therefore, the molecular ion of each product indicated a monoacetamidated ester, and the fragments specified the position of the acetamide group along the chain. The nmr spectra were also helpful in this regard. ω -1 substituted products gave a distinctive methyl doublet for the ω (terminal) methyl group. All other ω - n isomers would, of course, give a triplet. The entire nmr spectrum was in each case fully consistent with the proposed structure, as were elemental analyses and ir spectra.

Conditions suitable for producing acetamido ester were studied, using either methyl or ethyl butyrate. It was found that using an undivided cell (beaker) reduced the yield substantially. The reaction is not, however, sensitive to oxygen, since even bubbling oxygen through the anolyte did not change the yield significantly. Increasing the number of faradays/mole from 2 to 3 (divided cell) improved the yield from 21 to 53%. Increasing it to 4 faradays/mol did not, however, further increase the yield. Since the smaller acetamido esters are water soluble, the usual, simple extraction procedure removes some of this product. A continuous chloroform extraction of one mixture from an ethyl butyrate oxidation gave a total yield of 70%. The fate of the remainder of the reactant is not known. Some starting material is always found, but many of these reactants are relatively volatile and, if oxidation was not complete, large amounts would have been evaporated on work-up.

Several experiments were performed using tetraethylammonium fluoroborate electrolyte. In acetonitrile-fluoroborate background oxidation occurs at more anodic potentials than with perchlorate.⁷ At 2.75 V the background current was about 25 mA. Addition of methyl butanoate did not change this value appreciably. Oxidation for 140 min passed 2 faradays/mol and a 5% yield of the acetamido ester was formed. A small amount of ethyl 3-acetamidobutanoate was also detected. The ethyl group presum-

ably arose from the ammonium salt. Oxidation of ethyl butanoate in tetraethylammonium fluoroborate-acetonitrile was also performed at 3.10 V. The current was constant at 180 mA and a 15% yield of ethyl 3-acetamidobutanoate was produced along with several unidentified products. Similarly, methyl butanoate produced a 10% yield of the monoamide when oxidized at 3.00 V with lithium fluoroborate as electrolyte.

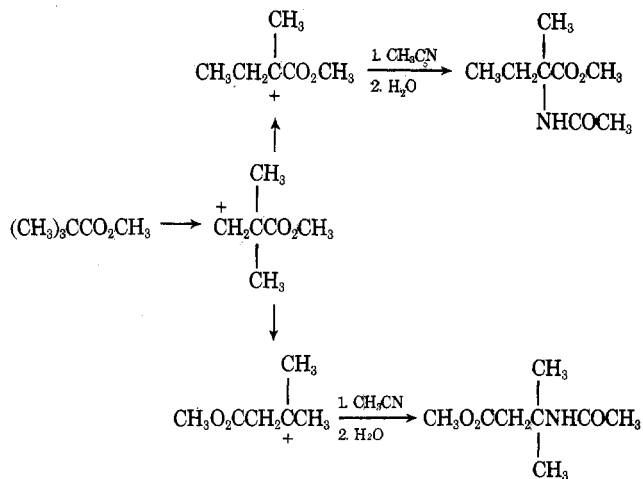
Discussion

The results summarized in Table II demonstrate that simple esters can be cleanly monoacetamidated. Straight-chain esters give preferential ω -1 substitution, *e.g.*



Thus, ethyl butyrate gave only the ω -1 product in yields as high as 70% when 3 faradays/mol was passed and continuous extraction of the product mixture from water into chloroform was employed. Methyl hexanoate gave primarily ω -1 and ω -2 products. Methyl nonanoate gave three major peaks on glc. One of these was identified by nmr as the ω -1 isomer. The technique is synthetically attractive because of this positional selectivity, the mild conditions, and clean reaction products. It should be applicable to many types of acyclic aliphatic compounds. Indeed, 2-methylpentane is acetamidated under these conditions.

The selectivity is reminiscent of ester chlorinations,⁸ especially those employing *N*-chloro amines in sulfuric acid.⁹ That reaction has been suggested to involve a radical chain mechanism.¹⁰ The anodic reaction, however, seems to involve carbonium ions. Acetonitrile adducts are presumptive evidence for carbonium ion precursors¹¹ *via* Ritter¹² type reactions. The substitution position can also be rationalized using carbonium ions. Thus, the most stable cation is formed in all cases. For straight chains that cation is at the secondary position, most remote from the electron-withdrawing ester function,¹³ and, as the chain becomes longer, more ω -2 product is observed. Finally, carbonium ion rearrangements are observed in suitable



cases. The oxidation of methyl 1,1-dimethylpropionate is, for example, thought to proceed *via* competing methyl and carbomethoxy migration¹⁴ to an unstable primary carbonium ion. The intermediacy of a free primary carbonium ion is, of course, unlikely, but, since alkyl radicals do not rearrange, a species resembling this unstable species seems necessary. This is the only case studied where *only* a primary carbonium ion is available by loss of hydrogen and it is also the only unequivocal case of rearrangement. Secondary-secondary carbonium ion rearrangements could be involved in many of the other examples, but

Table II
Anodic Products from Esters^a

Registry no.	Substrate	<i>n</i> , faraday/mol	Product	(% yield) ^b	Registry no.
	None	4	Succinonitrile, chlorine dioxide ^c		
105-54-4	Ethyl butanoate	2	Ethyl 3-acetamidobutanoate	(21)	43135-00-8
		3		(55)	
		4		(53)	
		4		(70) ^d	
		4		(10) ^e	
623-42-7	Methyl butanoate	4	Methyl 3-acetamidobutanoate	(49) ^f	43135-01-9
		3		(55)	
		3		(14) ^g	
		4		(15) ^h	
106-70-7	Methyl hexanoate	4	Methyl 5-acetamidohexanoate	(42)	43135-02-0
			Methyl 4-acetamidohexanoate	(11)	43135-03-1
1731-84-6	Methyl nonanoate	4	Methyl 8-acetamidononanoate	(25) ⁱ	43135-07-5
556-24-1	Methyl 3-methylbutanoate	3	Methyl 3-acetamido-3-methylbutanoate	(68)	43135-04-2
108-64-5	Ethyl 3-methylbutanoate	3	Ethyl 3-acetamido-3-methylbutanoate	(70)	43135-05-3
547-63-7	Methyl 2-methylpropionate	3	Methyl 2-acetamido-2-methylpropionate	(58)	43135-06-4
			Methyl 3-acetamidobutanoate	(4)	
598-98-1	Methyl 2,2-dimethylpropionate	3	Methyl 2-acetamido-2-methylbutanoate	(30)	43135-08-6
			Methyl 3-acetamido-3-methylbutanoate	(20)	
			Ethyl propionate	3	
	Diethyl methylmalonate	3	Diethyl methylmalonate		

^a Oxidations at 2.74 V vs. Ag/AgNO₃ using lithium perchlorate except where noted. ^b % yields and *n* based on added ester. ^c Identified by uv λ_{max} (CH₃CN) 358 nm. ^d Continuous extraction of products from water to chloroform. ^e Oxidation at 3.00 V using lithium fluoroborate. ^f Oxygen bubbled through the anolyte during the oxidation. ^g Oxidation in a beaker. ^h Oxidation at 3.10 V using tetraethylammonium fluoroborate. ⁱ Isomeric amides were present. Glc indicates that ω-2 and ω-3 are also major products.

those will not be exothermic like this primary-tertiary rearrangement. The relative migratory aptitude observed for methyl:carbomethoxy of 3:2 is, indeed, consistent with literature analogies.¹⁵ It is, however, expected that all the carbonium ions formed anodically would lead to alkenes as well as amides. We find no evidence for alkenes.

Although more detailed mechanistic experiments are called for, these results indicate that extremely unstable carbonium ions can be anodically generated under very mild conditions. Indeed, temperature is always an independent variable in electrochemistry. We have carried out the substitution of methyl butanoate at -40° with similar product yield.

Addition of substrate has a very small effect on the background current at 2.75 V for perchlorate or 3.35 V for fluoroborate electrolyte. Also, the current does not decay even though ester is being consumed. This implicates an indirect oxidation of ester and is in contrast to the oxidation of some other aliphatic compounds where direct electron transfer from substrate is implicated.^{2-4,7} In particular it contrasts with the oxidation of 1-carbomethoxyadamantane, which is converted to 3-acetamido-1-carbomethoxyadamantane.^{2,16} In other cases involving cyclic molecules which oxidize at potentials just below background, we have found complex mixtures of products and currents which decay with time. The difference may lie in the high oxidation potential of acyclic esters.¹⁶ Since methyl propionate and diethyl methylmalonate do not react, the reaction appears to be limited to esters where a dialkyl carbonium ion can be formed either directly or by rearrangement (e.g., in methyl 2,2-dimethylpropionate oxidation). In the perchlorate medium it is generally accepted that the perchlorate anion is being oxidized at 2.75 V.^{7,17} This is consistent with our results. It is also true, however, that perchlorate-derived species are not neces-

sary for amidation, since fluoroborate also works.¹⁸ The nature of the attacking species is not known, but it cannot be very stable since oxidation in perchlorate without substrate, followed by addition of substrate, gave succinonitrile, not acetamidated ester.

It is of interest to note that the oxidation in perchlorate background is so successful in producing products. It has been suggested that perchlorate media are less attractive than fluoroborate because the perchlorate is more reactive.¹⁷ This work demonstrates that this reasoning can be invalid for synthesis applications. It also shows that very similar chemistry results from what appears to be background and direct oxidations. This suggests common mechanistic attributes. These will be evaluated in the future.

Experimental Section

General. Starting material and products were analyzed as CDCl₃ solutions by nmr on a Varian T-60 instrument and chemical shifts are reported in δ units. Ir spectra were taken on a Perkin-Elmer 457 grating spectrometer. Mass spectra were recorded with an A.E.I. Model MS-12 spectrometer. Glc analyses were performed on a Model 720 F & M gas chromatograph equipped with thermal conductivity detectors. A 15 ft × 0.25 in. aluminum column packed with 15% Carbowax 20M on Chromosorb W, acid washed and HMDS treated, was used. Elemental analyses were performed by Chemalytics, Inc.

All the oxidations were carried out in a three-compartment cell.¹⁹ A Model 70HV 1/90 Wenking potentiostat was employed. A square wave pulse from a Model 126 Exact Sweep Generator was generally used. This pulsed the potential to ~0 V for 1 sec every 10 sec and provided high currents. The acetonitrile (Eastman) was distilled twice from P₂O₅ and stored under nitrogen and over Fischer 4A molecular sieves. Anhydrous lithium perchlorate (0.2 M, G. F. Smith Chemical Co.) was used as the electrolyte without purification. Dry nitrogen was continuously bubbled through the anode and cathode compartments. The cell was thermostated at room temperature during electrolysis. Most of the

oxidations were done at 2.74 V. The background current with LiClO_4 as the supporting electrolyte was found to vary anywhere between 120 to 250 mA at 2.75 V. Throughout the electrolysis period, the anolyte remained clear and colorless. The presence of water and absence of pulsing does not affect the yield of product. Rapid stirring of the anolyte during the electrolysis was achieved by a magnetic stirring bar. Usually the oxidation was performed for 3 hr. At the end, the anolyte was reduced to about 15 ml on a rotary evaporator. The residue was taken up in water and the organic products were extracted with chloroform. The extracts were combined and dried over anhydrous magnesium sulfate. The solution was filtered and evaporated to give a pale yellow to colorless, viscous oil. This material was then chromatographed on a silica gel column and eluted with Skelly, 50-50 Skellysolve-chloroform, and then with pure chloroform.

Oxidation of Methyl Butanoate. This ester (380 mg, 3.7 mmol) was oxidized at 2.74 V for 2 hr at a constant current of 170 mA; 330 mg of product was recovered as a colorless oil leading to an overall yield of 55% based on the initial amount of substrate added. Upon chromatographic purification, it produced a colorless solid melting at room temperature: ir (CHCl_3) 3440, 3000, 1725, 1670, 1510, 1440, 1370, 1230, 1200, 780, 720 cm^{-1} ; nmr δ 6.2 (broad, 1 H), 4.38 (m, 1 H), 3.68 (s, 3 H), 2.54 (d, 2 H), 1.96 (s, 3 H), 1.23; mass spectrum m/e (rel intensity) 43 (100), 86 (40), 102 (20), 116 (20), 159.

Anal. Calcd for $\text{C}_7\text{H}_{13}\text{NO}_3$: C, 52.84; H, 8.175; N, 8.804. Found: C, 52.72; H, 8.08; N, 8.60.

Oxidation of Methyl Hexanoate. Oxidation of this ester (450 mg, 3.5 mmol) at 2.74 V and at a constant current of 220 mA for 3 hr gave 390 mg of product. Upon glc, mass spectral, and nmr analysis this was found to contain 80% of the (ω -1) amido ester and 20% (ω -2) amido ester. The overall yield of the reaction was found to be 53%. The two isomers were separated by glc at a column temperature of 210°. The major product was identified from the following data: ir (CHCl_3) 3440, 3000, 1740, 1665, 1515, 1440, 1365, 1262-1200 (broad), 780-700 cm^{-1} (broad); nmr δ 5.8 (broad, 1 H), 4.0 (m, 1 H), 3.7 (s, 3 H), 2.38 (m, 2 H), 2.0 (s, 3 H), 1.6 (m, 4 H), 12.0 (d, 3 H); mass spectrum m/e (rel intensity) 43 (100), 86 (76), 114 (66), 144 (30), 187.

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{NO}_3$: C, 57.75; H, 9.09; N, 7.487. Found: C, 57.99; H, 8.84; N, 7.51.

The minor product was identified from the following data: ir (CHCl_3) 3440, 3000, 1740, 1665, 1515, 1440, 1365, 1262-1200 (broad), 780-700 cm^{-1} (broad); nmr (CDCl_3) δ 5.4 (broad, 1 H), 3.9 (m, 1 H), 3.62 (s, 3 H), 2.38 (t, 2 H), 2.00 (s, 3 H), 1.9-1.2 (m, 4 H), 0.9 (t, 3 H); mass spectrum m/e 84, 58, 116, 126, 114, 158, 100, 187.

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{NO}_3$: C, 57.75; H, 9.09; N, 7.487. Found: C, 57.52; H, 9.25; N, 7.31.

Oxidation of Methyl 3-Methylbutanoate. Oxidation at 2.74 V and 140 mA for 150 min gave 448 mg (68%) of the crude product. Upon chromatographic purification it produced a colorless oil which eventually crystallized at slightly below the room temperature: ir (CHCl_3) 3440, 3000, 1726, 1670, 1515, 1440, 1370, 1300, 1225 cm^{-1} (broad); nmr (CDCl_3) δ 6.36 (broad, 1 H), 3.66 (s, 3 H), 2.86 (s, 2 H), 1.96 (s, 3 H), 1.4 (s, 6 H); mass spectrum m/e (rel intensity) 58 (100), 43 (77), 116 (34), 100 (16), 173.

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{NO}_3$: C, 55.50; H, 8.67; N, 8.09. Found: C, 54.98; H, 8.67; N, 7.95.

Oxidation of Ethyl 3-Methylbutanoate. This ester (503 mg, 3.8 mmol) was oxidized at 2.74 V at a constant current of 200 mA for 105 min; 510 mg of crude acetamido ester was isolated accounting for an overall yield of 70%. Upon chromatographic purification it produced a colorless oil: ir (CHCl_3) 3440, 3000, 1720, 1665, 1510, 1440, 1370, 1225 (broad), 810-710 cm^{-1} (broad); nmr (CDCl_3) δ 6.1 (broad, 1 H), 4.18 (q, 2 H), 2.74 (s, 2 H), 1.96 (s, 3 H), 1.43 (s, 6 H), 1.26 (t, 3 H); mass spectrum m/e 58, 130, 100, 142, 187.

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{NO}_3$: C, 57.75; H, 9.09; N, 7.487. Found: C, 57.61; H, 9.02; N, 7.56.

Oxidation of Methyl Butanoate with Fluoroborate Electrolyte. This ester (325 mg, 3.2 mmol) was oxidized at 3.10 V with tetraethylammonium tetrafluoroborate as the electrolyte at a constant current of 40 mA; 108 mg of the product was isolated. The product was found to contain a mixture of two compounds. From comparison of the nmr and mass spectra one was identified as methyl 2-acetamidobutanoate and the other was identified as ethyl 2-acetamidobutanoate.

Oxidation of Ethyl Butanoate. Ethyl butanoate (454 mg, 3.9 mmol) was oxidized at 2.76 V at a constant current of 300 mA for 150 min; 362 mg of the product was isolated which amounted to

53% yield based on the starting material. Upon chromatographic purification it produced a colorless, viscous oil. Smaller numbers of faradays/mol gave lower yields (Table I) and a continuous extraction of the aqueous phase with chloroform gave an additional 115 mg of product.

Oxidation of 460 mg in a 250-ml beaker was accomplished with a stainless steel cathode, the usual platinum anode, and a reference electrode separated from the electrolysis medium with a glass frit. The yield of product was 14%: nmr (CDCl_3) δ 6.33 (broad, 1 H), 4.2 (q, 2 H), 2.5 (d, 2 H), 1.96 (s, 3 H), 1.28 (t, 3 H), 1.2 (d, 3 H); mass spectrum m/e (rel intensity) 43 (100), 86 (35), 116 (20), 130 (15), 173.

Oxidation of Methyl 2-Methylpropionate. This ester (491 mg, 4.8 mmol) was oxidized at 2.74 V and 180 mA for 195 min and produced 464 mg (64%) of the product. The major component (95% of total) was identified from the following data: ir (CHCl_3) 3450, 3000, 1730, 1675, 1505, 1450, 1385, 1365, 1300 (broad), 905, 800-700 cm^{-1} (broad); nmr (CDCl_3) δ 6.28 (broad, 1 H), 3.72 (s, 3 H), 1.98 (s, 3 H), 1.53 (s, 6 H); mass spectrum m/e 100, 58, 102, 159.

Anal. Calcd for $\text{C}_7\text{H}_{13}\text{NO}_3$: C, 52.84; H, 8.175; N, 8.80. Found: C, 53.24; H, 8.53; N, 8.89.

The minor product (<5% of the total) was identified as methyl 2-acetamidobutanoate by glc coinjection with an authentic sample and mass spectra.

Oxidation of Methyl 2,2-Dimethylpropionate. This ester (451 mg, 3.9 mmol) was oxidized at 2.74 V at a constant current of 190 mA for 135 min; 344 mg of the product was isolated which amounted to 51% overall yield based on the initial amount of substrate added. The major product (60% of the total) was identified as methyl 2-acetamido-2-methylbutanoate by comparison (nmr spectra and glc coinjection) with an authentic sample. The minor product (40%) was identified from the following data: nmr (CDCl_3) δ 6.33 (broad, 1 H), 3.8 (s, 3 H), 2.0 (m, 4 H), 1.6 (s, 3 H), 1.8 (t, 3 H); mass spectrum m/e 72, 102, 114, 173.

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{NO}_3$: C, 55.5; H, 8.67; N, 8.09. Found: C, 55.65; H, 8.55; N, 8.59.

Oxidation of Methyl Nonanoate. This ester (1.046 g, 6.1 mmol) was oxidized at 2.74 V at a constant current of 400 mA for 90 min; 800 mg (55%) of crude product was isolated. Three major components were identified by glc and nmr showed that one of these was the (ω -1) product.

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Registry No.—Acetonitrile, 75-05-8.

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