Acta Chemica Scandinavica, 1999: 53: 792–799
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Electrochemical Reductive Coupling Reactions of Aliphatic Nitroalkenes

Peter Mikesell, Michael Schwaebe, Marcello DiMare and R. Daniel Little*

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, CA 93106, USA

Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

Mikesell, P., Schwaebe, M., DiMare, M. and Little, R. D., 1999. Electrochemical Reductive Coupling Reactions of Aliphatic Nitroalkenes. – Acta Chem. Scand. 53: 792–799. © Acta Chemica Scandinavica 1999.

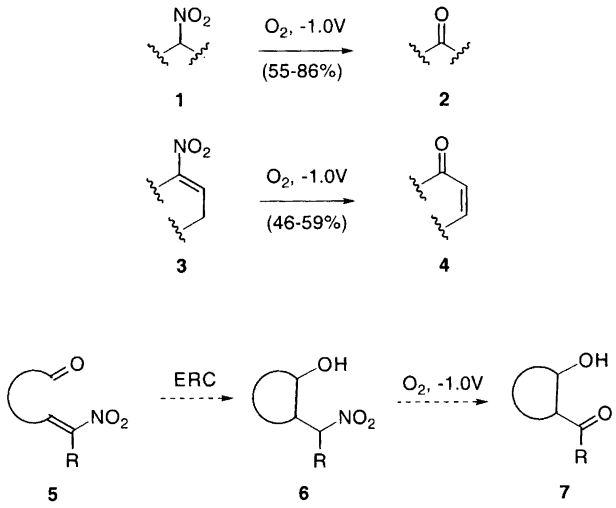
We describe how to *selectively* affect *either* β-to-β coupling (electrohydrodimerization) or coupling between the α and β centers of aliphatic nitroalkenes, the latter in a catalytic process that can be initiated both with and without electrochemistry. Of particular significance is our discovery of conditions that allow electrohydrodimerization to be conducted *using aliphatic nitroalkenes bearing acidic protons*. Thus, one can affect at will, either a catalytic α-to-β coupling or an electrohydrodimerization using substrates that bear acidic protons, as well as those that do not. We also describe both voltammetric and ESR studies of the simple 1-nitro-3,3-dimethyl-1-butene, as well as the results of quantum mechanical calculations that shed light upon the nature of radial anions derived from electron deficient olefins. Both calculation and experiment suggest that the reluctance of these materials to undergo electrohydrodimerization can be correlated with the low electron density on carbon and the corresponding high value on oxygen, of the radical anion.

Nitroalkenes are interesting and useful materials. Much of their chemistry focuses upon their ability to serve as Michael acceptors and cycloaddition partners.[1] Their redox behavior has also been studied extensively, particularly reductions leading to a variety of products (e.g., oximes and amines), depending upon reaction conditions.[2]

Some time ago, we demonstrated that in the presence of electrochemically generated superoxide, secondary nitroalkanes are converted into the corresponding ketones (**1** to **2**).[3] Subsequently, we examined the behavior of secondary nitroalk*enes* under similar conditions and discovered that they could be converted into the corresponding α,β-unsaturated ketones in modest yield (**3** to **4**; 46–59%).[4]

Recently, our interest turned to the possibility that a nitroalkene might serve as a coupling partner in an electroreductive cyclization reaction (e.g., **5** to **6**),[5] the thought being that the cyclic nitroalkane product **6** could subsequently be oxidized as indicated above, thereby allowing the preparation of aldol like adducts **7**.

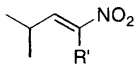
To prepare for this effort, we first elected to explore the electrochemistry of a series of aliphatic nitroalkenes, **8a**–**8g**, under conditions typically used for the electroreductive cyclization (ERC) process.[5] It was hoped that



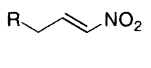
nitroalkenes would be useful in electrohydrocyclization (EHC) and electrohydrodimerization (EHD) reactions as well.[6] Because nitroalkenes are reduced so easily (e.g., −1.3 V), the reductions might prove selective in the presence of other, more difficult to reduce functionalities (enones, enoates, unsaturated nitriles, etc.).

From our investigation we have learned how to *selectively* affect *either* β,β-coupling (electrohydrodimerization, e.g., **8** to **10**) or coupling between the α and β centers (**8**

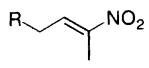
* To whom correspondence should be addressed.



8a, R' = H
8e, R' = CH_3



8b, R = *n*-Bu
8c, R = Et
8f, R = $BnO(CH_2)_2$
8g, R = $PhCH_2$



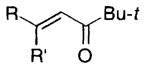
8d, R = Et

to **11**), the latter in a catalytic process that can be initiated both with and without electrochemistry.[7] Of particular significance is our discovery of conditions that allow electrohydrodimerization to be conducted *using aliphatic nitroalkenes bearing acidic protons.*[8] We also describe both voltammetric and ESR studies of the simple system 1-nitro-3,3-dimethyl-1-butene (**9**), as well as the results of quantum mechanical calculations that shed light upon the nature of radical anions derived from electron deficient olefins.

Results and discussion

Previous reports by Schäfer and Wessling demonstrated the suitability of aryl and heteroaryl substituted nitroalkenes in the electrohydrodimerization process.[8] Those bearing acidic hydrogens at the γ position, however, present a special challenge in that they display a propensity to undergo acid–base chemistry preferentially. To circumvent this problem, 1-nitro-3,3-dimethyl-1-butene (**9**) was chosen as a substrate for investigation since the γ site is blocked. Its redox behavior is illustrated by a fully reversible cyclic voltammogram at each of the scan rates examined (Fig. 1). From voltammetry we estimated the half-life of the radical anion to be greater than 10 min.[9] This was refined to 12–15 min by examining the decay of its UV absorption, and was further corroborated by ESR spectroscopy (Fig. 2; 0.2 M Bu_4NBF_4, CH_3CN, no added proton donor). Using a modified flat cell, substrate **9** was reduced directly in an ESR cavity at room temperature. The decay of the signal was measured with respect to time, and extrapolation of the data led to measurements of 12.6 to 15.4 min. An accurate *g*-value of 2.00473 was measured using 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) as an internal standard;[10] the hyperfine coupling constants were found to be $a_N = 19.6$, $a_{\beta\text{-H}} = 13.7$, $a_{\alpha\text{-H}} = 3.5$, and $a_{\text{Bu-}t} = 0.5$ G.

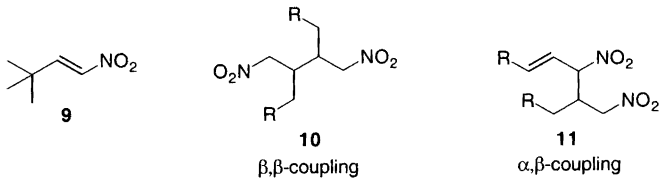
The observed species is believed to be the radical anion of **9**, rather than the protonated radical based upon its CV curve. If the protonated radical were present, it would be expected to undergo reduction more readily than the starting material. This would be manifest in the resulting CV curve; it was not. The long half-life of the radical anion of **9** contrasts dramatically with a value of > 10 s that is observed for the analogous enones **12** and **13** in dry DMF,[9,11] and is reflected by diminished reactivity toward all processes but reverse electron transfer.



12, R = Bu-*t*, R' = H
13, R = H, R' = Bu-*t*

It was clear at this point that nitroalkenes were not likely to behave in a manner analogous to that of other electron deficient olefins. To gain insight into the nature of the differences between nitroalkene radical anions and those derived from other electron deficient alkenes, calculations were performed at the UMP2/6-31 + G** level on the radical anions of the nitroalkene **14**, as well as the α,β-unsaturated aldehyde, ketone, and nitrile, **15**–**17**, respectively (Table 1).[12]

Comparison of the SOMO coefficient at the carbon β



9

10
β,β-coupling

11
α,β-coupling

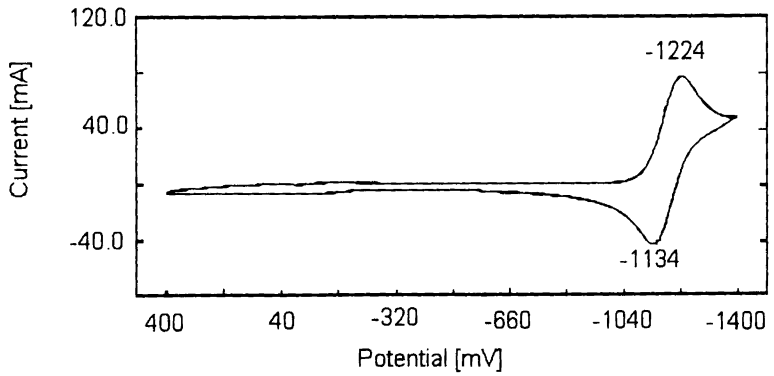


Fig. 1. CV curve of **9** (500 mV s^{-1}).

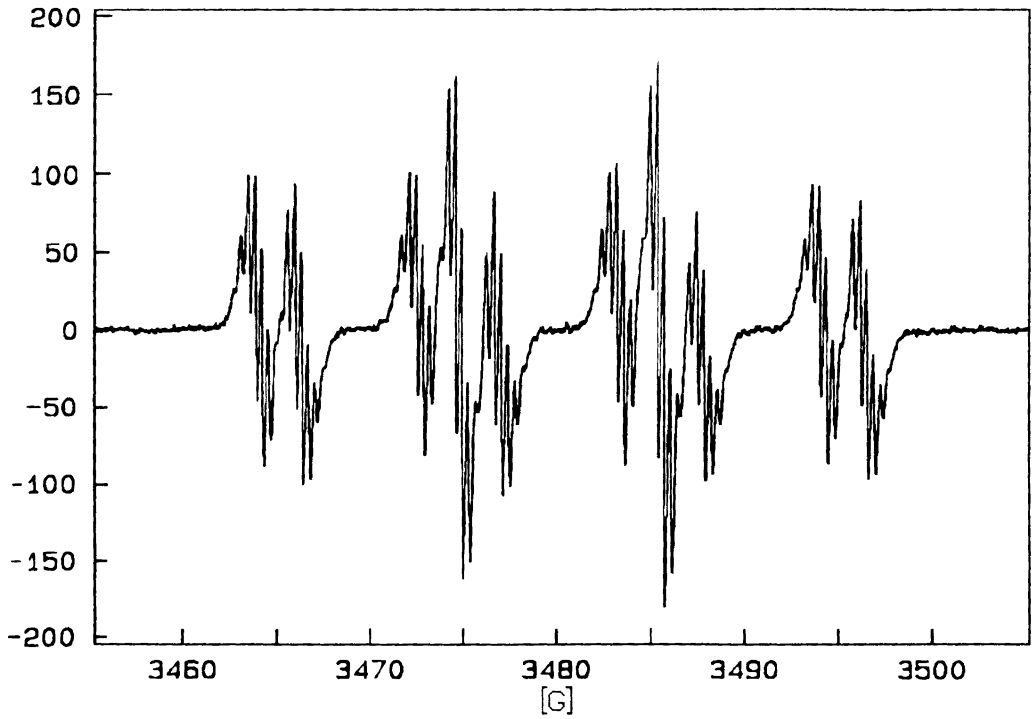
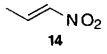
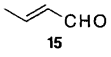
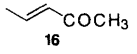


Fig. 2. ESR spectrum of $\mathbf{9}^{-\cdot}$.

Table 1. SOMO coefficients of activated alkenes.

				
	14	**15**	**16**	**17**
c_r (SOMO)	−0.672	0.993	1.047	1.321
$\pi_{total}(c_r)$	0.958	1.148	1.182	1.383

to the electron withdrawing group, c_r, and the total π-density at that site, reveals that both parameters decrease in the order cyano > aldehyde ≈ ketone > nitro. If the tendency to couple is associated with electron density at the β-carbon, then this information suggests that the nitro group ought to be the least likely to do so. In fact, the calculations show that the bulk of the electron density is associated with oxygen [e.g., for **14**, $c_{oxygen}(SOMO) = 2.04$]. These predictions were corroborated by a trapping experiment in which nitroalkene **18** was reduced in the presence of acetic anhydride. In principle, this material could undergo intramolecular coupling between the β-carbons of the unsaturated ester and nitroalkene subunits (electrohydrocyclization). Instead, the *O*-acetylated adduct **19** was isolated in 68% yield. This behavior contrasts sharply with that of the α,β-unsaturated keto ester **20**. When it was reduced under very similar conditions, acylation occurred at the β-carbon to afford **21**, rather than on oxygen.[13]

Synthesis of aliphatic nitroalkenes. The electrochemistry of six additional aliphatic nitroalkenes, **8a**–**8g**, was examined. Unlike **9**, these materials possess acidic hydrogens at the γ-carbon. Each was synthesized by using a Henry reaction followed by acylation and elimination, as illustrated in the equation located above Table 2. Both potassium *tert*-butoxide in *t*-BuOH–THF as well as sodium methoxide in methanol were used successfully as base–

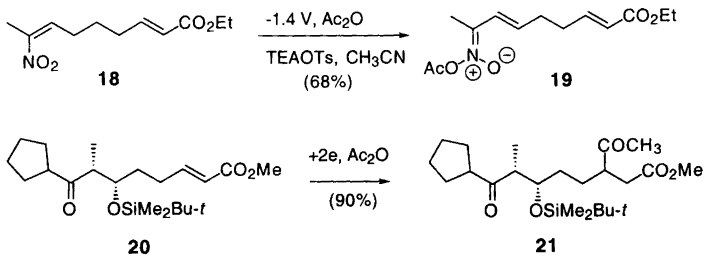
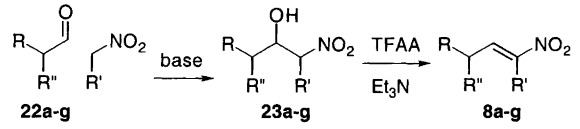


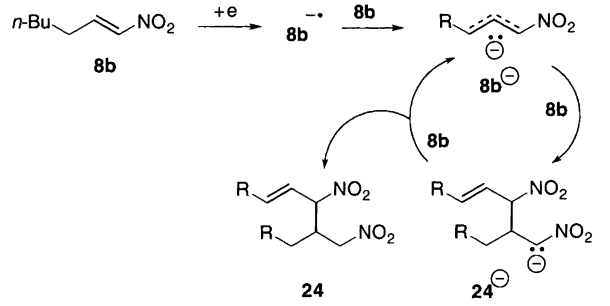
Table 2. Formation of nitroalkenes.



Series	R	R″	R′	Yield **23** (%)	Yield **8** (%)	Base
a	Me	Me	H	73	64	KOBu-*t*
b	*n*-Bu	H	H	99	75	KOBu-*t*
c	Et	H	H	76	68	MeONa
d	Et	H	Me	70	53	KOBu-*t*
				84	74	MeONa
e	Me	Me	Me	63	61	KOBu-*t*
f	$BnO(CH_2)_2$	H	H	95	71	KOBu-*t*
g	$Ph(CH_2)_2$	H	H	—	30	KOBu-*t*

solvent combinations.[14] The latter was sometimes preferred as it proved easier to remove the lower boiling solvent. Elimination may be carried out on the crude nitro alcohol; however, better yields than those listed in Table 2 (≈90%) are obtained if purified material is employed. The elimination is sensitive to the amount of triethylamine in the reaction mixture; excess amine leads to α,β-dimerization (cf. **8b** to **24**). With the careful addition of trifluoroacetic anhydride and triethylamine, nitroalkenes can be isolated in large quantities (ca. 3.5 g).

Electrochemistry – divided cell. The first electrolyses were carried out in a divided cell (H-type) under a controlled potential of −1.31 V vs. SCE, using a mercury pool cathode and a platinum anode. The solvent was acetonitrile with 0.01 M tetrabutylammonium tetrafluoroborate as the electrolyte. TLC analysis of the reaction with **8b** showed a total consumption of starting material after only 5% of the necessary current had been delivered. At this point the current dropped to zero indicating that the consumption of **8b** was the result of a catalytic acid–base reaction. Two stereoisomers of **24** were obtained in 76% yield. These materials were independently synthesized by the addition of a catalytic amount of triethylamine to **8b** in methylene chloride. Of interest is the fact that coupling occurs exclusively between the α and β centers to afford the β,γ-unsaturated product, **24**, rather than the α,β-unsaturated isomer that would have resulted from coupling between the γ and β centers. This result parallels the normal kinetic preference for



alkylation/protonation at the α site of enolates derived from α,β-unsaturated ketones, esters, etc.[15]

The catalytic cycle is almost certainly initiated by the abstraction of the γ-proton of the nitroalkene **8b** by its radical anion **8b**$^{-\cdot}$, the so-called electrogenerated base (EGB).[16] The resulting carbanion **8b**$^-$ conjugatively adds to **8b** to afford **24**$^-$, which is quenched by the starting material to afford the product, **24**, regenerate **8b**$^-$, and continue the cycle.

The presence of a variety of proton donors (*viz.*, *t*-BuOH, water, phenol) during the electrochemical experiments failed to quench the cycle. When dimethyl malonate was added as a potential proton donor, both the coupled product **24** and that resulting from the conjugate addition of dimethyl malonate to the starting material were observed. The use of a more acidic proton donor (HOAc) converted **8b** into the corresponding oxime **25** (94%).

Electrochemistry – single cell. The results cited thus far clearly point to the reluctance of aliphatic nitroalkenes to undergo electrohydrodimerization, as predicted by the small SOMO coefficient at the β carbon of the radical anion (see Table 1). We are pleased to report that this coupling mode *can* be achieved simply by increasing the current density.[17,18] This was accomplished by using a single rather than a divided cell. It was reasoned that the formation of a high local concentration of radical anions might lead to preferential coupling of two such intermediates, rather than acid–base chemistry, since the latter requires a reaction between two *different* species (*viz.*, the radical anion and starting material). Regardless of the nature of the intermediate(s) or the absence of detailed mechanistic study, this modification provided the desired outcome. The results are shown in Table 3. For reasons that are not clear, yields are substantially

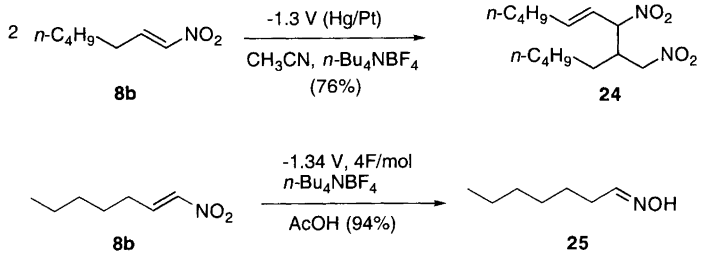
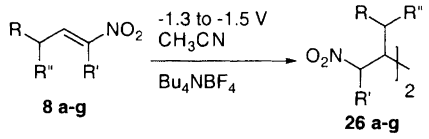


Table 3. Electrohydrodimerization of nitroalkenes.



Substrate	R	R′	R″	Yield (%)
8a	CH_3	H	CH_3	71
8b	*n*-Bu	H	H	74
8c	Et	H	H	70
8d	Et	CH_3	H	44
8e	CH_3	CH_3	CH_3	41
8f	$BnO(CH_2)_2$	H	H	41
8g	$Ph(CH_2)_2$	H	H	95

reduced with α-substituted nitroalkenes **8d** and **8e**. Furthermore, with these substrates, it was necessary to use a magnesium, rather than a platinium anode.

Further evidence that current density is a critical parameter in determining the regiochemical outcome of the coupling process was found by conducting the electrolysis in a single cell with the electrodes positioned as far apart as the apparatus would allow (ca. 4 cm), in this case, a simple 500 ml three-necked round-bottomed flask. The increased distance between the electrodes served to raise the resistance and thus lower the current density; the potential was monitored independently. The result was dramatic. With nitroalkene **8b** a complete reversal of regiochemistry was observed, the α,β-dimer **24** being isolated in 95% yield.

A typical experiment simply calls for the use of a three-necked round-bottomed flask equipped with a nitrogen inlet, graphite rod cathode, Pt anode, and an Ag/AgCl reference electrode with the electrodes positioned as close to one another as is practical. Following degassing (nitrogen) and a pre-electrolysis of the supporting electrolyte/solvent system (−1.34 V until the background current drops to less than 2 mA; 0.01 M Bu_4NBF_4 dissolved in acetonitrile), the substrate is added. Reduction at −1.34 to −1.50 V, depending upon the substrate, proceeds smoothly with the consumption of 1 F mol^{-1}.

Concluding remarks

Nitroalkenes *are* versatile materials. We believe that the results described above make them even more so. The stage has been set to explore their behavior as electroreductive cyclization substrates. At this point, one can affect at will, either a catalytic α-to-β coupling or an electrohydrodimerization using substrates that bear acidic protons, as well as those that do not. Both calculation and experiment suggest that the reluctance of these materials to undergo electrohydrodimerization can be correlated with the low electron density on carbon and the corresponding high value on oxygen, of the radical anion.

Experimental

General. ^1H NMR spectra were recorded at 200, 400 or at 500 MHz, and ^{13}C NMR spectra were recorded at 50 MHz. All spectra were recorded for samples in $CDCl_3$, and chemical shifts are reported in δ relative to TMS. IR spectra of solid compounds were obtained as solutions in $CDCl_3$ (NaCl plates). Solvents were dried (drying agent in parentheses) and distilled prior to use: Et_2O and THF (Na–benzophenone); CH_2Cl_2 and Et_3N (CaH_2). Thin-layer chromatography (TLC) was performed using precoated glass plates; Kieselgel 60 GF_{254} (Merck). Column chromatography was performed using ICN (32–63, 60 Å) silica gel and the indicated solvents reported by volume (v/v). Capillary gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph. All reactions were conducted under an argon atmosphere. Spectral data for each compound is listed below, and the relevant procedure is cited next to the compound name/number.

General procedure for the synthesis of nitro alcohols using potassium tert*-butoxide (procedure A).*[14] To an oven-dried round-bottomed flask fitted with a Teflon-coated stirring bar were added THF and *tert*-butanol (1:1). The aldehyde (1 equiv.) was added, followed by nitromethane (or nitroethane, 1.5 equiv.) and potassium *tert*-butoxide (20 mol%). The mixture was allowed to stir overnight and quenched with saturated ammonium chloride. The aqueous layer was extracted with ether (2 × 20 ml), and the combined organic extracts were washed with brine, dried over magnesium sulfate, and the solvent was removed *in vacuo*. The resulting oil was chromatographed on silica gel (10:90 ether–pentane) affording, as a clear oil, nitro alcohols of type **23** in the yields listed in Table 2.

General procedure for synthesis of nitroalkenes from nitro alcohols (procedure B).[14] Nitroalcohols (1 equiv.) were dissolved in methylene chloride and trifluoroacetic acid anhydride (1.05 equiv.) was added dropwise during which the reaction was cooled in an ice–water bath under an argon atmosphere. Triethylamine was then added dropwise (2.10 equiv.), and the reaction mixture was allowed to stir for an additional 30 min. The reaction was quenched with ammonium chloride, and the organic layer was extracted twice with methylene chloride. The combined organic extracts were washed with sodium bicarbonate, brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the resulting yellow oil chromatographed on silica gel (5:95 ether–pentane) affording the nitroalkenes as pale yellow oils in the yields listed in Table 2.

Alternative procedure for the synthesis of nitroalkenes; use of sodium methoxide (procedure C). The aldehyde (69.4 mmol) was combined with 104.1 mmol nitromethane (or nitroethane). Methanol (30 ml) was added, followed by the addition of 0.75 g (13.9 mmol) of sodium

methoxide. The solution was allowed to stir overnight after which time it was poured into water and extracted three times with ether. The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure (5 Torr) to afford the desired nitro alcohol in 70–80% yield. The crude nitro alcohol (52.5 mmol) was diluted with 53 ml of methylene chloride and cooled in an ice–water bath. Trifluoroacetic anhydride (7.51 ml, 52.5 mmol) was added dropwise, and the resulting solution was allowed to stir for 2 min after which time 14.6 ml (104.9 mmol) of triethylamine were carefully added *dropwise* over 20 min. The solution was allowed to stir for an additional 30 min, washed with an aqueous solution of saturated ammonium chloride, and dried over sodium sulfate. The organic layer was concentrated under reduced pressure, and purified by column chromatography (ether in petroleum ether) to afford the desired nitroalkene in the yields listed in Table 2.

Procedure for divided-cell electrolysis; dimethyl malonate as proton donor (procedure D). To an oven-dried H-cell was added a degassed solution of 0.01 M tetrabutylammonium tetrafluoroborate in acetonitrile. Dimethyl malonate (5 equiv.), a mercry pool (2 cm diameter × 0.5 cm pool), and a Teflon-coated platinum wire were added to the cathodic chamber. A silver/silver chloride reference electrode was positioned about 0.5 cm above the mercury surface. A platinum anode was placed in the anodic chamber, and the contents were pre-electrolyzed until the background current dropped to an acceptable level (0.2 mA, ca. 3 min). Nitroalkene **8b** (1 equiv.), dissolved in acetonitrile (final concentration ca. 0.03 to 0.07 M), was added and the electrolysis was carried out until the current returned to the background level. The catholyte was poured into a separatory funnel containing ether (50 ml) and saturated ammonium chloride (20 ml). The aqueous layer was extracted with ether (2 × 20 ml), and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated *in vacuo*. The resulting oil was chromatographed on silica gel (5:95 ether–pentane) to afford the compound resulting from the conjugate addition of malonate anion to the nitroalkene.

General procedure for single-cell electrolysis (procedure E). To a 250-ml Erlenmeyer flask was added a 0.01 M solution of tetrabutylammonium tetrafluoroborate in acetonitrile. A graphite cathode, platinum anode (magnesium anode for α-substituted nitroalkenes), and silver/silver chloride reference electrode were positioned so that the average distance between all electrodes was about 1 cm. Pre-electrolysis was conducted with constant degassing until the background current dropped to 0.2 mA. The substrate was introduced (final concentration ca. 0.01 to 0.07 M), and electrolyzed at −1.34 V (−1.50 V for α-substituted nitroalkenes) until the current returned to 0.2 mA. The solvent was removed *in vacuo* and the salts were removed by filtration through silica gel, eluting with ether. The resulting oil was chromatographed on silica gel (5:95 ether–pentane) to afford dimers of type **26** in the yields listed in Table 3.

General procedure for divided-cell electrolysis (procedure F). An oven-dried H-cell was allowed to cool under a nitrogen atmosphere. Tetrabutylammonium tetrafluoroborate in acetonitrile (50 ml, 0.01 M) was added to the cell. The cell was equipped with with a Ag/AgCl (referenced to SCE) reference electrode, mercury pool cathode, and a platinum anode. The solution was degassed (N_2, 15 min), followed by pre-electrolysis at −1.34 V until the background current was less than 2 mA. The nitroalkene (1.47 mmol) was added and the electrolysis was carried out until the current dropped to less than 0.2 mA (0.37 F mol^{-1} consumed). The solution was concentrated under reduced pressure, filtered through a pad of silica gel with ether, and concentrated to afford dimer **24**.

Procedure for oxime formation (procedure G). An oven-dried H-cell was allowed to cool under a nitrogen atmosphere. Tetrabutylammonium tetrafluoroborate in acetonitrile (0.01 M) was dried by being stirred over alumina for 5 min. Approximately 50 ml of the solution were filtered into an H-cell, followed by the addition of 1.0 ml of glacial acetic acid. The cathodic compartment was equipped with an Ag/AgCl (referenced to SCE) reference electrode, and mercury was the working electrode (platinum anode). The solution was degassed (N_2, 15 min), followed by pre-electrolysis at −1.34 V until the background current was less than 2 mA. Nitroalkene **8b** (1.40 mmol) was added and the electrolysis was carried out until the current dropped to less than 2 mA (4 F mol^{-1} consumed). The solution was poured into a separatory funnel and diluted with 50 ml of saturated aqueous sodium bicarbonate. The product was extracted three times with 25 ml of methylene chloride and once with ether. The combined organic layers were concentrated under reduced pressure, filtered through a pad of silica gel with ether, and concentrated to afford 1.38 mmol of oxime **25** (94%).

3-Methyl-1-nitrobut-1-ene (**8a**). Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (dd, J=7.20, 7.20 Hz, 1 H), 7.98 (d, J=13.60, 1 H), 3.63 (app d sext, J=6.80, 1.60 Hz, 1 H), 2.19 (d, J=7.20 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 138.1, 28.2, 20.9. IR (NaCl, neat): 2968, 2878, 1648, 1527, 1466, 1350, 1160, 965 cm^{-1}.

1-Nitrohept-1-ene (**8b**). Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dt, J=13.20, 7.60 Hz, 1 H), 6.99 (d, J=14.00 Hz, 1 H), 2.26 (q, J=7.20 Hz, 2 H), 1.56 (quintet, J=7.60 Hz, 2 H), 1.33 (m, 2 H), 0.91 (t, J=7.20 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 139.5, 31.1, 28.3, 27.3, 22.2, 13.8.

1-Nitropent-1-ene (**8c**). Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (dt, J=13.20, 7.60 Hz, 1 H), 6.99 (d, J=13.60 Hz, 1 H), 2.26 (q, J=8.00 Hz, 2 H), 1.56 (sextet, J=7.60 Hz, 2 H), 0.99 (t, J=7.60 Hz, 3 H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 139.6, 30.3, 21.0, 13.6. IR (NaCl, neat): 3099, 2962, 2929, 2868, 1642, 1519, 1455, 1350, 955, 461 cm^{-1}. MS: m/z 116 $(P+1)^+$, 74, 49. HRMS: Calc. for $C_5H_{10}NO_2$: 116.071154. Found: 116.071633.

2-Nitrohex-2-ene (**8d**). Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (t, J=7.60 Hz, 1 H), 2.22 (q, J=7.20 Hz, 2 H), 2.17 (s, 3 H), 1.55 (sextet, J=7.60 Hz, 2 H), 0.98 (t, J=7.20 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 136.1, 29.9, 21.7, 13.7, 12.4. IR (NaCl, neat): 2963, 2875, 1521, 1455, 1389, 1334 cm^{-1}. MS: m/z 130 $(P+1)^+$ 83, 71, 55, 43. HRMS: Calc. for $C_6H_{12}N_1O_2$: 130.086804. Found: 130.086781.

4-Methyl-2-nitropent-2-ene (**8e**). Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, J=10.4 Hz, 1 H), 2.59 (m, 1 H), 2.18 (s, 3 H), 1.11 (d, J=6.80 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 100.0, 27.9, 21.7, 12.4. IR (NaCl, neat): 2970, 2888, 1726, 1637, 1523, 1461, 1386, 1336, 1287, 1170, 1008 cm^{-1}. MS: m/z 130 $(P+1)^+$ 127, 114, 111, 83, 71, 59, 55, 43. HRMS: Calc. for $C_6H_{12}N_1O_2$: 130.086804. Found: 130.087264.

(5-Nitropent-4-enyloxymethyl)benzene (**8f**). Procedure C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.24 (m, 5 H), 6.97 (app t, J=1.60 Hz, 1 H), 6.94 (app t, J=1.20 Hz, 1 H), 4.50 (s, 2 H), 3.50 (t, J=6.00 Hz, 2 H), 2.38 (q, J=7.60 Hz, 2 H), 1.81 (q, J=6.40 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 139.7, 138.0, 128.4, 127.7, 127.6, 73.0, 68.6, 27.8, 25.3. IR (neat, NaCl): 3033, 2938, 2862, 1649, 1524, 1451, 1354, 1267, 1106, 910 cm^{-1}.

(4-Nitrobut-3-enyl)benzene (**8g**). Procedure A and B. IR (neat): 3102, 3085, 3062, 3027, 2929, 2859, 1768, 1733, 1648, 1523, 1454, 1351, 952, 750, 700 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.24 (m, 6 H), 6.95 (dt, J=1.7, 13.5 Hz, 1 H), 2.83 (m, 2 H), 2.58 (m, 2 H). ^{13}C NMR (50 MHz): 141.4, 139.9, 139.9, 128.7, 128.2, 126.6, 33.8, 30.0. MS: 178 $(P+H)^+$, 144, 133, 117, 105, 91.

3,3-Dimethyl-1-nitrobut-1-ene (**9**). Procedure A and B. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.28 (d, J=13.50 Hz, 1 H), 6.91 (d, J=13.50 Hz, 1 H), 1.17 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.7, 136.9, 32.4, 28.1. IR (neat): 3120, 2966, 2869, 1643, 1529, 1496, 1351 cm^{-1}.

7-Nitro-8-nitromethyltridec-5-ene (**24**). Procedure F. The two diastereomers may be separated by column chromatography (10% ether in pentanes, R_f=0.62 and 0.58). The spectral data for each follow.

R_f=0.58: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (q, 1 H, J=7.50 Hz), 5.57 (t, J=10.50 Hz, 1 H), 5.48 (t, J=8.50 Hzm 1 H), 4.57 (dd, J=15.50 Hz, 1 H), 4.43 (dd, J=20.00, 5.00 Hz, 1 H), 2.82 (m, 1 H), 2.20 (m, 2 H), 1.4–1.3 (br m, 12 H), 0.89 (m, 6 H). IR (NaCl, neat): 2931, 2865, 1555, 1458, 1370, 794 cm^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 120.6, 85.4, 74.4, 40.7, 31.3, 31.0, 27.6, 25.9, 22.2, 13.8, 13.7.

R_f=0.62: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (q, 1 H, J=8.00 Hz), 5.59 (t, J=10.00 Hz, 1 H), 5.49 (t, 1 H, J=7.00 Hz), 4.52 (dd, J=15.50 Hz, 1 H), 4.42 (dd, J=15.00 Hz, 6.00 Hz 1 H), 2.87 (m, 1 H), 2.15 (m, 2 H), 1.4–1.3 (br m, 12 H), 0.90 (m, 6 H). IR (NaCl, neat): 2931, 2865, 1555, 1458, 1370, 794 cm^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 120.3, 84.3, 74.9, 40.8, 31.4, 31.0, 27.6, 27.4, 25.8, 22.2, 13.8, 13.7.

Electrohydrodimer **26a**. Procedure E. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.48–4.32 (m, 4 H), 2.43–2.40 (m, 2 H), 1.85–1.81 (m, 2 H), 1.06–0.84 (m, 12 H).

Electrohydrodimer **26b**. Procedure E. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.42–4.32 (m, 4 H), 2.41 (m, 2 H), 1.48–1.21 (m, 16 H), 0.90 (br d s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 31.5, 31.4, 28.3, 28.0, 26.7, 26.6, 22.3, 22.2, 13.8. IR (NaCl, neat): 2930, 2864, 1553, 1455, 1374, 909, 735 cm^{-1}.

Electrohydrodimer **26c**. Procedure E. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39 (m, 4 H), 2.41 (m, 2 H), 1.4–1.26 (m, 8 H), 0.95 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 76.7, 38.1, 30.0, 20.1, 13.7.

Electrohydrodimer **26d**. Procedure E. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.70–4.55 (m, 2 H), 2.10 (m, 2 H), 1.59–1.48 (m, 4 H), 1.37–1.31 (m, 4 H), 1.25 (m, 6 H), 0.97–0.87 (m, 6 H).

Electrohydrodimer **26f**. Procedure E. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 128.3, 127.7, 127.6, 73.0, 69.2, 38.2, 27.1, 24.8. IR (NaCl, neat): 2939, 2863, 1730, 1552, 1454, 1366, 1108, 742 cm^{-1}.

Electrohydrodimer **26g**. Procedure E. IR (neat): 3085, 3062, 3027, 2929, 2859, 1733, 1648, 1523, 1454, 1351 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.21, (m, 10 H), 4.37 (dd, J=2.20, 6.30 Hz, 4 H), 2.54 (m, 6 H), 1.66 (m, 4 H). ^{13}C NMR (50 MHz): δ 140.1, 128.7, 128.5, 128.3, 128.2, 126.6, 76.4, 38.1, 33.2, 30.2. MS: m/z 309, 231, 215, 178, 117, 91.

Heptanal oxime (**25**). Procedure G. The following data are from a mixture of stereoisomers (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, 1 H, J=6.00 Hz), 6.72 (t, 1 H, J=5.60 Hz), 2.38 (q, 2 H, J=7.70 Hz), 2.20 (q, 2 H, 6.40 Hz), 1.49 (m, 3 H), 1.30 (m, 12 H), 0.88 (m, 6 H). IR (NaCl, neat): 3260, 3114, 2928, 2860, 1714, 1460, 1377, 934, 732 cm^{-1}. MS: m/z 130 $(P+1)^+$, 128, 112, 97, 83, 69, 55. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 152.3, 31.5, 29.4, 29.0, 28.7, 26.5, 26.0, 25.0, 22.5, 14.0.

8-Nitronona-2,7-dienoic acid ethyl ester (**18**). Procedure A and B. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.12 (t, J=

7.60 Hz, 1 H), 6.94 (dt, J=6.90 Hz, 15.70 Hz, 1 H), 5.86 (d, J=15.70 Hz, 1 H), 4.20 (q, J=7.00 Hz, 2 H), 2.29 (m, 4 H), 2.17 (s, 3 H), 1.71 (m, 2 H), 1.29 (t, J= 7.00 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.2, 147.9, 147.3, 135.0, 122.2, 60.1, 31.4, 27.2, 26.5, 14.1, 12.4.

*8-(Acetyl-*aci*-nitro)nona-2,6-dienoic acid ethyl ester* (**19**). IR (neat): 2979, 2933, 2856, 1766, 1720, 1650, 1446, 1367, 1268, 1197 cm^{-1}. ^{1}H NMR (200 MHz): δ 6.92 (dt, J=6.4, 15.70 Hz, 1 H), 6.24 (m, 2 H), 5.37 (d, J= 15.70 Hz, 1 H), 4.11 (q, J=7.10 Hz, 2 H), 2.31 (m, 4 H), 2.12 (s, 3 H), 2.01 (s, 3 H), 1.21 (t, J=7.10 Hz, 3 H). ^{13}C NMR (50 MHz): δ 168.4, 166.2, 161.9, 147.0, 138.7, 127.1, 122.0, 60.1, 31.0, 30.8, 19.5, 14.1, 11.2.

2-(1-Nitromethylhexyl)malonic acid diethyl ester. Procedure D. IR (neat, NaCl): 2969, 1745, 1731, 1554, 1475, 1382, 1178 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.72 (dd, J=4.90, 13.30 Hz, 1 H), 4.54 (dd, J=6.90, 13.30 Hz, 1 H), 4.23 (q, J=7.30 Hz, 4 H), 3.64 (d, J= 5.90 Hz, 1 H), 2.90 (m, 1 H), 1.25–1.45 (m, 8 H), 1.29 (t, J=7.30 Hz, 6 H), 0.89 (t, J=6.20 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.9, 167.7, 79.8, 61.8, 54.5, 36.8, 31.3, 29.9, 26.2, 22.7, 13.27, 13.3. MS: m/z 258, 212, 197, 183, 160, 133, 109, 95, 55.

Use of cyclic voltametry to estimate the half-life of the radical anion derived from **9**.[9] The scan rate was varied until i_{pa}/i_{pc}=0.50 (i_{pa} and i_{pc} are the anodic and cathodic currents, respectively). The time necessary for the scan to travel from the cathodic peak to the anodic peak is measured ($t=\Delta V/v$, where ΔV is the magnitude of the potential scanned between the cathodic and anodic peaks, and v is the scan rate). When i_{pa}/i_{pc}=0.50, then half of the reduced material is present at the electrode surface at the time of the anodic wave, and t is the time needed for half of the material to decay. Although this method is intuitively appealing, it provides values that are 2–4 times shorter than the universally accepted Nicholson and Shain method.[19,20]

References

1. Denmark, S. E. and Thorarensen, A. *Chem. Rev. 96* (1996) 137.
2. Wessling, M. and Schäfer, H. J. *Chem. Ber. 124* (1991) 2303.
3. Little, R. D., Monte, W. T. and Baizer, M. M. *J. Org. Chem. 48* (1983) 803.
4. Little, R. D., Baizer, M. M., Sugawara, M., Monte, W. T. and Hess, U. *Acta. Chem. Scand., Ser. B 37* (1983) 509.
5. Little, R. D. and Schwaebe, M. K. In: Steckhan, E., Ed., *Topics in Current Chemistry*, Springer-Verlag, New York 1997, Vol. 185, p. 1.
6. Baizer, M. M. and Anderson, J. D. *J. Electrochem. Soc. 111* (1964) 223.
7. Little, R. D., Schwaebe, M., Russu, W. In: Torri, S., Ed., *Novel Trends in Electroorganic Synthesis*, Kodansha Ltd., Tokyo 1995, p. 123.
8. Schäfer, H. J. and Wessling, M. *Elektrochemische Stoffgewinnung 23* (1992) 807.
9. For a detailed discussion, refer to House, H. O., Bowers, K. W., Giese, R. W., Grimshaw, J., Kolodny, N. H., Kronberger, K. and Roe, D. K. *J. Am. Chem. Soc. 92* (1970) 2783. Using the methodology described in this paper, the scan rate is varied until the ratio of the anodic and cathodic peak currents i_{pa}/i_{pc}=0.50; i_{pc} is related to the concentration of the anion radical initially produced, c_0, while i_{pa} is related to the concentration of the radical anion remaining in the layer surrounding the electrode at the time of reoxidation, c_t. The time to scan from the cathodic peak to the anodic peak is measured using the relationship, t= [potential difference]/scan rate=ΔV/v). When i_{pa}/i_{pc}=0.50, this is approximated to be the time required for the initial concentration of the radical anion to decay to one-half its original value.
10. Nelsen, S. F. In: Kochi, J. K., Ed., *Free Radicals*, Wiley, New York 1973, Vol. 2, Ch. 21.
11. Little, R. D. and Baizer, M. M. In: Patai, S., Rappoport, Z., Eds., *The Chemistry of Enones Part 2*, John Wiley, New York 1989, p. 599.
12. Hehre, W. J., Radom, L., Schleyer, P. V. R. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York 1986.
13. Sowell, C. G. *Ph.D. Dissertation*, University of California, Santa Barbara, CA 1990.
14. Denmark, S. E. and Marcin, L. R. *J. Org. Chem. 58* (1993) 3850.
15. House, H. O. *Modern Synthetic Reactions*, Benjamin, Menlo Park 1972, p. 502.
16. Utley, J. H. P. In: Steckhan, E., Ed., *Topics in Current Chemistry*, Springer-Verlag, New York 1987, Vol. 142, p. 131.
17. Matzeit, A., Schäfer, H. J. and Amatore, C. *Synthesis* (1995) 1432.
18. Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd ed., Wiley-Interscience, New York 1989, p. 7.
19. Nicholson, R. S. and Shain, I. *Anal. Chem. 36* (1964) 706.
20. Nicholson, R. S. and Shain, I. *Anal. Chem. 37* (1965) 178.

Received October 7, 1998.