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Electrogenerated Superoxide-Initiated Autoxidation. A Convenient Electrochemical Method for the Conversion of Secondary Nitroalkanes to Ketones and the Use of Primary Nitroalkanes as Acyl Anion Equivalents in Michael Reactions[†]

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Electrochemically generated superoxide ion was used as a base to deprotonate secondary nitroalkanes whose anions were then oxidized with molecular oxygen, thereby providing a means of converting the secondary nitro group to a ketone. In addition, the radical anion of azobenzene was used as an electrogenerated base to catalyze the Michael condensation of primary nitroalkanes with a variety of acceptors; subsequent exposure of the Michael adduct to the electrogenerated superoxide-initiated autoxidation provides a one-pot sequence for the β-addition of an acyl anion equivalent.

Of the many methods that can be utilized for the construction of 1,4-dicarbonyl compounds,[1] some involve the use of nitro compounds whose role is to function either as a donor (i.e., as the nucleophile) or as an acceptor (e.g., a nitroalkene) in Michael condensation reactions. A recent report by Clark and Cork that delineates the use of nitronate anions in a direct, one-pot synthesis of 1,4-diketones[2] prompts us to report the use of significantly different methodology that we have utilized to achieve similar objectives. Our work was stimulated by two factors, namely, an interest in novel applications of the Michael reaction[3] and an interest in the development and use of electrochemical methodology in organic synthesis.[4]

Initial efforts focused upon the development of an alternative means of achieving the conversion of a nitro group into a carbonyl unit. While there exists a reasonable variety of methods that can serve to accomplish this transformation,[5] we were interested in developing a simple and efficient electrochemically based method. To achieve this objective, we decided to use molecular oxygen and to take advantage of the fact that it can be readily reduced to afford superoxide ion, which, in turn, can behave as a base capable of abstracting protons from carbon acids whose pK_a is ca. 25 or less.[6] Thus, our plan called for the use of superoxide as an electrogenerated base (an EGB) whose role was to abstract a proton from a nitroalkane, thereby affording a nitronate anion, which would then undergo oxidation in the presence of molecular oxygen.[7]

$$\mathrm{O_2} \xrightarrow{-1.0\ \mathrm{V\ (SCE)}} \mathrm{O_2}^{-\bullet}$$

$$\mathrm{RR'C{=}O} \Longleftarrow \mathrm{RR'CHNO_2} + \mathrm{O_2} + \mathrm{O_2}^{-\bullet}$$

In practice, a stream of oxygen was passed through a gas dispersion tube that was inserted into the cathode chamber of a standard H cell containing a mercury pool as the working electrode, tetra-*n*-butylammonium bromide as the supporting electrolyte, and the nitroalkane of choice dissolved in acetonitrile. To form superoxide, the potential was set and maintained at −1.0 V vs. SCE, thereby providing a very convenient means of reducing molecular oxygen. Each reaction was monitored by coulometry and, in several cases, by gas chromatography. Workup was initiated after the passage of 1 faraday of current. From the examples illustrated in Table I, it is clear that the methodology can be used to effect the desired functional group change.[8]

To determine whether the nitrogen-containing byproduct of the autoxidation corresponded to nitrite or to nitrate ion, a standard qualitative analysis sequence was conducted. The presence of nitrite was first determined by the observation of a positive starch–iodide test when the catholyte was acidified with a nonoxidizing[9] solution of 3 M sulfuric acid. The result was confirmed by the

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[†] Electrogenerated Bases. 5. For paper 4, see ref 6b.

[‡] Alfred P. Sloan Foundation Fellow, 1980–1984.

[1] For a reasonably extensive compilation of references dealing with the synthesis of 1,4-dicarbonyl compounds as well as another useful method to accomplish this transformation, see Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679–4681. For an interesting and useful electrochemical method, see Shono, T.; Nishiguchi, I.; Ohmizu, H. *Ibid.* **1977**, *99*, 7936.

[2] Clark, J. H.; Cork, D. G. *J. Chem. Soc., Chem. Commun.* **1982**, 635–636.

[3] (a) Little, R. D.; Dawson, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 4607. (b) Little, R. D.; Dawson, J. R. *Tetrahedron Lett.* **1980**, 2609–2612. (c) Little, R. D.; Verhé, R.; Monte, W. T.; Nugent, S. T.; Dawson, J. D. *J. Org. Chem.* **1982**, *47*, 362–364.

[4] Nugent, S. T.; Baizer, M. M.; Little, R. D. *Tetrahedron Lett.* **1982**, *23*, 1339–1342. Little, R. D.; Carroll, G. L. *J. Org. Chem.* **1979**, *44*, 4720–4722.

[5] Nolan, W. E. *Chem. Rev.* **1955**, *55*, 137. Shecter, H.; Williams, F. T., Jr. *J. Org. Chem.* **1962**, *27*, 3699. McMurry, J. E.; Melton, J. *J. Am. Chem. Soc.* **1971**, *93*, 5309; *J. Org. Chem.* **1973**, *38*, 4367. Kornblum, N.; Wade, P. A. *Ibid.* **1973**, *38*, 1418. McMurry, J. E.; Melton, J.; Padgett, H. *Ibid.* **1974**, *39*, 259. Jacobson, R. *Tetrahedron Lett.* **1974**, *3215*. Russell, G. A. *J. Am. Chem. Soc.* **1954**, *76*, 1595. Bartlett, P. A.; Green, F.; Webb, T. R. *Ibid.* **1977**, 331. Williams, J. W.; Unger, L.; Moore, R. H. *J. Org. Chem.* **1978**, *43*, 1217. Keinan, E.; Mazur, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3861. Galobardes, M.; Pinnick, H. W. *Tetrahedron Lett.* **1981**, *22*, 5235. Olah, G.; Arvanghi, M.; Vankar, Y. D.; Prakash, G. K. S. *Synthesis* **1980**, 662–663. Olah, G. A.; Gupta, B. G. *Ibid.* **1980**, 44. Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1. Cookson, R. C.; Ray, P. S. *Tetrahedron Lett.* **1982**, *23*, 3521–3524.

[6] (a) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393–400 and references therein. (b) Allen, P. M.; Hess, U.; Foote, C. S.; Baizer, M. M. *Synth. Commun.* **1982**, *12*, 123–129. (c) For an excellent and enlightening discussion dealing with the effect of structure on the rate of reaction of carbanions with molecular oxygen, see Russell, G. A.; Moye, A. J.; Nagpal, K. *J. Am. Chem. Soc.* **1962**, *84*, 4145–4155.

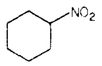
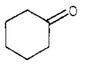
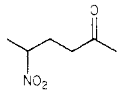
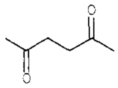
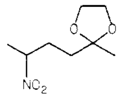
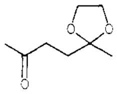
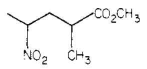
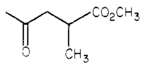
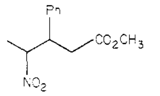
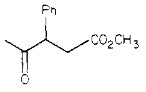
[7] The enzyme-catalyzed reaction of superoxide anion with 2-nitropropane to generate acetone and nitrite anion has been reported by Kido, T.; Soda, K.; Asada, K. *J. Biol. Chem.* **1978**, *253*, 266. We are grateful to a referee for this reference.

[8] Russell has shown that the sodium salt of 2-nitropropane absorbs oxygen at room temperature in 0.5–0.6 M aqueous sodium hydroxide to afford acetone and nitrite ion. A "small amount" of cyclohexanone was produced from the sodium salt of nitrocyclohexane under the same conditions. The sodium salt of phenylnitromethane displayed no reactivity toward oxygen at 25 °C, even in the presence of ferric salts. We were curious to determine whether a switch from the counterion and solvent used by Russell to that used in the electrochemical transformation would allow one to accomplish the functional group change under nonelectrochemical conditions. As indicated in the Experimental Section, this was indeed the case. However, among other things, the time required to effect the change was significantly longer than that required for the electrochemical process. Further studies of this reaction are planned. See Russell, G. A. *J. Am. Chem. Soc.* **1954**, *76*, 1595–1600.

[9] Margolis, E. J. "Qualitative Anion-Cation Analysis"; Wiley: New York, 1962.

0022-3263/83/1948-0803$01.50/0

Table I

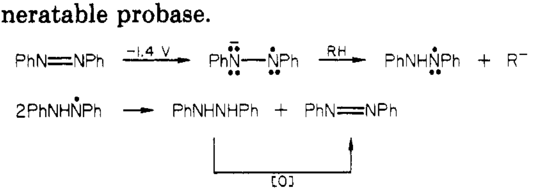
entry	substrate	faradays	time, h	product	yield, %
1		1.0	2.5		55[a]
2		1.0	2.0		70 (92)[b]
3		1.0	2.0		82-86
4		1.0	1.0		71
5		1.0	1.0		76 (98)[b]
6		1.0	0.6		68, 15% recovered starting material

[a] Reaction carried out in DMF; product isolated as the 2,4-DNPH derivative. [b] Reaction run in acetonitrile; yields refer to distilled cyclohexanone in the first instance and to a GC yield in the second. In general, a yield shown in parentheses refers to a GC yield, while all other yields refer to pure, isolated products.

formation of the characteristic red ferrithiocyanate complex, $Fe(SCN)^{2+}$, upon exposure of the catholyte to a solution of thiourea in acetic acid followed by treatment with ferric chloride. It should be noted that *nitrite* and *not nitrate* is capable of undergoing this confirmatory reaction. Qualitative tests designed to detect the presence of nitrate proved negative.[9]

We next turned our attention toward the development of methodology designed to provide a means of achieving a one-pot Michael condensation between a nitronate anion and a Michael acceptor, followed by conversion of the nitro group of the resulting adduct to a carbonyl unit. In practice, the radical anion of azobenzene was used as an electrogenerated base to effect the condensation, while the autoxidation reaction described above was used to effect the desired functional group change.

Azobenzene can be reduced to afford either the corresponding radical anion (at -1.4 V) or the dianion (at -1.8 V); either species can function as an electrogenerated base.[10] When the radical anion is used, the byproducts include hydrazobenzene was well as azobenzene, which forms via disproportionation of the radical anion once it has abstracted a proton from, for example, a carbon acid whose pK_a is ca. 25 or less. In several instances, the hydrazobenzene has been reconverted to azobenzene anodically.[10] Therefore, azobenzene can be thought of as a regeneratable probase.

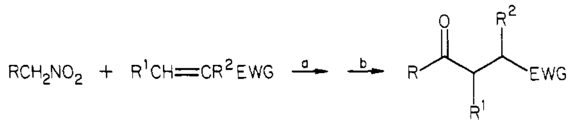


$$PhN{=}NPh \xrightarrow{-1.4\ V} Ph\ddot{N}{-}\dot{\ddot{N}}Ph \xrightarrow{RH} PhNH\dot{\ddot{N}}Ph + R^-$$

$$2PhNH\dot{N}Ph \longrightarrow PhNHNHPh + PhN{=}NPh$$

In the present investigation, azobenzene was utilized in catalytic quantities to promote the conversion of a nitroalkane to a nitronate anion that undergoes Michael condensation in the presence of a suitable acceptor. Upon completion of the reaction, as determined by the disappearance of the Michael acceptor (GC analysis), a gas dispersion tube was lowered into the catholyte, oxygen was bubbled through the solution, and the reduction was carried out at -1.0 V as described above.

The overall transformation is illustrated in the equation shown below and the results are summarized in Table II.



EWG = electron-withdrawing group; a, PhN=NPh (cat.), -1.4 V (SCE), 0.2 N $(n\text{-}Bu)_4NBr$, CH_3CN; b, O_2, -1.0 V (SCE), 0.2 N $(n\text{-}Bu)_4NBr$, CH_3CN.

With the exception of entries 3, 5, and 6, the yields for the sequence average close to 60%. The time required to accomplish the transformation using ethyl cinnamate (entry 3) is significantly longer than any of the other cases due to its slow rate of reaction as a Michael acceptor under the present reaction conditions (cf. entry 6 of Table I with entry 3 of Table II). As is illustrated by entries 5 and 6, no reaction is observed when the β-carbon of the Michael acceptor is sterically hindered.

In summary, electrogenerated superoxide ion was used as a base to deprotonate secondary nitroalkanes whose anions were then oxidized with molecular oxygen, thereby providing a means of converting the secondary nitro group to a ketone. One of the attractive features of this reaction is that a single reagent, molecular oxygen, serves a dual role as both the precursor to superoxide ion and as an oxidant of the nitronate anion. In addition, the radical anion of azobenzene was used as an electrogenerated base to catalyze the Michael condensation of primary nitroalkanes with a variety of acceptors; subsequent exposure of the Michael adduct to the electrogenerated superoxide-initiated autoxidation provides a one-pot sequence for the β-addition of an acyl anion equivalent. Further studies are in progress.

Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. Nitroethane, methyl methacrylate, methyl crotonate, cyclopentenone, ethyl cinnamate, pulegone, isophorone, and azobenzene were used directly as the commerically available materials (Aldrich). Other nitro compounds that were utilized were prepared according to the literature references that are cited. Tetra-*n*-butylammonium bromide (electrometric grade) was purchased from Southwestern Analytical Chemicals, Inc. and was used as received. Reactions were carried out in spectral grade acetonitrile (Mallinkrodt), which was filtered through activated alumina (ca. 40 g/120 mL of solvent, Sigma, neutral alumina) prior

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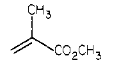
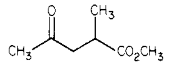
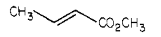
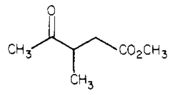
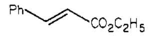
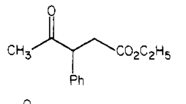
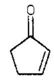
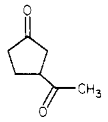
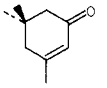
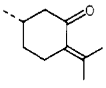
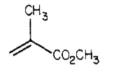
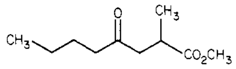
(10) For previous examples dealing with the use of electrogenerated bases in Michael reaction, see (a) White, D. A.; Baizer, M. M. *Tetrahedron Lett.* **1973**, 3597–3600. (b) Baizer, M. M.; Chruma, J. L.; White, D. A. *Ibid.* **1973**, 5209–5212.

Table II

entry	nitroalkane	Michael acceptor	time,[b] h	product	yield, %
1	$CH_3CH_2NO_2$		8		60
2	$CH_3CH_2NO_2$		7		59
3	$CH_3CH_2NO_2$		22		46[c]
4	$CH_3CH_2NO_2$		4		57
5	$CH_3CH_2NO_2$		19	no reaction[a]	
6	$CH_3CH_2NO_2$		19	no reaction[a]	
7	$CH_3(CH_2)_4NO_2$		6		62

[a] With 3,5,5-trimethylcyclohexenone, 82% of the starting material was recovered; with pulegone, 96% was recovered. [b] Time required for *both* reactions. [c] Compare with Table I, entry 6.

to use. Molecular oxygen (Linde, 99.3%) was passed through a glass tube (2 × 30 cm) packed with Drierite and sodium hydroxide pellets and then through 10-Å molecular sieves (Sigma) before passing through the gas dispersion tube and into the cathode compartment. Products were purified by distillation or by chromatography, using (a) a gravity flow silica gel column (Merck, silica 60, 70–230 mesh) and eluting with mixtures of ether in hexane, (b) a Chromatotron (Harrison Research, Model 7924) equipped with a 2-mm-thick silica gel rotor (Merck, silica 60 PF-254) and eluting with ether/Skellysolve F mixtures (FMI Model RP SY pump), or (c) an Aerograph A90-P3 preparative GC unit equipped with a 0.25 in. × 1.5 m 5% SE-30 column (column temperature, 150 °C). In cases a and b, phosphomolybdic acid (PMA, Aldrich) and/or a UV hand lamp was used in conjunction with TLC analysis to monitor the course of the chromatography.

A Hewlett Packard 5830A gas chromatograph equipped with the HP 18850 data system and a $^1/_8$ in. × 0.5 m 6% SE-30 column was used for analytical GC analysis. Infrared spectra were recorded neat, unless otherwise indicated, with a Perkin-Elmer 283 spectrometer. Proton NMR spectra were recorded with a Varian T-60 spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were recorded with a VG ZAB-2F spectrometer.

Electrochemical Equipment. All reactions were carried out under an argon atmosphere in a predried H cell. A medium-porosity glass frit separated the anode and cathode chambers. The cathode chamber was equipped with standard taper joints for the insertion of a cold-finger condenser to trap volatile components, an oxygen inlet tube (glass frit), and a luggin capillary-type reference electrode. A 706-mm^2 surface area mercury pool was used as the cathode, a 625-mm^2 platinum foil as the anode, and a saturated calomel electrode (SCE) as the reference electrode. All reductions were accomplished with a Wenking 70HV1/90 potentiostat. The reactions were monitored by coulometry with an Electrosynthesis 640 digital coulometer.

General Procedure for the Superoxide-Initiated Autoxidation of Nitroalkanes. Tetra-*n*-butylammonium bromide (60 mL each for the anode and the cathode chambers of the H cell) dissolved in acetonitrile was degassed with argon (5 min) and was then preelectrolyzed at −1.9 V until the background current dropped to less than 1 mA. Cyclohexene (1 mL) was added to the anolyte to react with any bromine formed during the electrolysis. The nitroalkane of choice was added to the catholyte, oxygen was bubbled through the solution, and the electrolysis was carried out at a constant potential of −1.0 V until loss of the starting material was indicated by analytical GC analysis. Upon completion of the reaction, the catholyte was removed and the cathode chamber was rinsed with ether. Unless otherwise indicated ca. 80% of the solvent was removed with a rot-o-vap under water aspirator pressure. Ether was added, and the combined organic solutions were washed with water and brine. After drying ($MgSO_4$), filtration, and concentration in vacuo, the material was purified. The data for each transformation are listed in the following order: amount of starting material, duration of reaction, number of faradays consumed, mode of product purification, and yield.

Cyclohexanone. Nitrocyclohexane[11] (1.78 g, 13.8 mmol); 2.0 h; 1.0 faraday; catholyte was distilled at atmospheric pressure without extraction. Cyclohexanone was collected in fractions boiling between 148 and 157 °C; 70% distilled yield (92% GC yield based upon the use of acetophenone as an internal standard; 1-m 15% SE-30 column).

Methyl 2-Methyl-4-oxopentanoate.[12a] Methyl 2-methyl-4-nitropentanoate[12b] (0.49 g, 2.8 mmol); 2.0 h; 1 faraday; preparative GC; 76% (98% GC yield, using biphenyl as an internal standard on a 0.5-m 6% SE-30 column). ^{1}H NMR δ 3.68 (s, 3 H, methyl ester), 2.87 (m, 3 H, ketone methylene and ester methine), 2.16 (s, 3 H, ketone methyl), 1.18 (d, 3 H, CH_3 α to ester).

2,5-Hexanedione. 5-Nitro-2-hexanone[12b] (415 mg, 2.86 mmol); 1.0 h; 1 faraday, preparative GC; 82–86%. ^{1}H NMR δ 2.7 (s, 4 H, methylene H's), 2.18 (s, 6 H, methyl H's).

Methyl 4-Oxo-3-phenylpentanoate.[13] Methyl 4-nitro-3-phenylpentanoate[12b] (0.51 g, 2.2 mmol); 0.6 h; 1 faraday, column chromatography, using 25% ether in hexane; 68% keto ester and 15% starting material. IR 3060, 2960, 1740–1710, 1600 cm^{-1}; MS, *m/e* 206 (parent), 164, 131, 121, 104, 77, 43; ^{1}H NMR δ 7.15 (s, 5 H, aryl), 4.12 (X of ABX, 1 H, J_{AX} = 9.7, J_{BX} = 5.4 Hz, methine), 3.1 (A of ABX, 1 H, J_{AB} = 17, J_{AX} = 9.7 Hz), 2.4 (B of ABX, 1 H, J_{AB} = 17, J_{BX} = 5.4 Hz), 3.58 (s, 3 H, ester methyl), 2.08 (s, 3 H, methyl).

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(11) Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659–661.

(12) (a) Boehmn, I.; Hirsch, E.; Reissig, H. U. *Angew. Chem.* **1981**, *93*, 593–594. (b) McMurry, J. E.; Melton, J. *J. Org. Chem.* **1973**, *38*, 4367–4373.

(13) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4927–4928.

2,5-Hexanedione Ethylene Ketal. 5-Nitro-2-hexanone ethylene ketal[12b] (0.36 g, 1.9 mmol); 1.0 h; 1 faraday; Kugelrohr distillation; 71%. ^{1}H NMR δ 3.85 (s, 4 H, ketal methylenes), 2.46 (m, 2 H, CH_2), 2.1–1.87 (m, 2 H, CH_2), 2.1 (s, 3 H, methyl α to ketone), 1.30 (s, 3 H, methyl).

General Procedure for the One-Pot Michael Superoxide Autoxidation. Each of the reactions were carried out in the standard H cell described above. The nitroalkane of choice and a catalytic amount (ca. 0.002 mmol) of azobenzene dissolved in acetonitrile were added to the cathode chamber, and the azobenzene was reduced at a constant potential of −1.4 V. The Michael acceptor was added dropwise via syringe and the resulting solution was stirred at room temperature until the acceptor was consumed as determined by GC analysis. After completion of the Michael reaction, the gas inlet tube was lowered into the catholyte and molecular oxygen was bubbled through the solution. Electrolysis was carried out at a constant potential of −1.0 V until 1 faraday of current was passed or until the starting material had reacted completely. The workup was identical with that described above for the autoxidation reaction. The data for each run is listed in the following order: amount of nitroalkane used, amount of Michael acceptor used, time required to effect the transformation, method of purification, yield.

Methyl 2-Methyl-4-oxopentanoate.[12a] Nitroethane (1.0 g, 13.3 mmol); methyl methacrylate (1.3 g, 13.3 mmol); 7.5 h, preparative GC; 60%; spectral data reported above.

Methyl 3-Methyl-4-oxopentanoate.[13] Nitroethane (0.34 g, 3.4 mmol); methyl crotonate (0.25 g, 3.4 mmol); 7 h, column chromatography, using 25% ether in hexane; 59%. ^{1}H NMR δ 3.67 (s, 3 H, methyl ester), 3.20–2.33 (m, 3 H, methylene and methine), 2.23 (s, 3 H, ketone methyl), 1.17 (d, 3 H, $J = 7$ Hz, CH_3 β to ester).

3-Acetylcyclopentanone. Nitroethane (0.45 g, 6.0 mmol); cyclopentenone (0.5 g, 6.0 mmol); 4 h; column chromatography, using 40% ether in hexane; 57%. IR 1730, 1710 cm^{-1}; ^{1}H NMR δ 2.27 (s, 3 H, CH_3); MS, *m/e* 126, 98, 83, 70, 55, 43. Anal. Calcd for $C_7H_{10}O_2$: 126.0681. Found: 126.0685.

Ethyl 4-Oxo-3-phenylpentanoate.[13] Nitroethane (0.20 g, 2.67 mmol); ethyl cinnamate (0.47 g, 2.67 mmol); 22 h; column chromatography, using 46% ether in hexane; 46% product and 6% recovered starting material. ^{1}H NMR δ 7.27 (s, 5 H, aryl), 4.12 (X of ABX, 1 H, $J_{AX} = 9.7$, $J_{BX} = 5.4$ Hz, methine), 4.10 (q, 2 H, $J = 7$ Hz, CH_2 of ethyl ester), 3.1 (A of ABX, 1 H, $J_{AB} = 17$, $J_{AX} = 9.7$ Hz), 2.4 (B of ABX, 1 H, $J_{AB} = 17$, $J_{BX} = 5.4$), 4.10 (q, 2 H, $J = 7$, CH_3CH_2O), 2.13 (s, 3 H, methyl), 1.2 (t, 3 H, $J = 7$, ester methyl).

Methyl 2-Methyl-4-oxooctanoate.[14] 1-Nitropentane (0.339 g, 2.9 mmol); methyl methacrylate (0.290 g, 2.9 mmol); 6 h; Chromatotron using 10% ether in Skellysolve F; 62%. ^{1}H NMR δ 3.67 (s, 3 H, methyl ester), 3.07–2.20 (m, 5 H, methine plus methylenes at C_3 and C_5), 1.77–1.0 (m, 4 H, methylenes of C_6 and C_7), 1.17 (d, 3 H, $J = 6$ Hz, C_2 methyl), 0.95 (ill-defined t, 3 H, $J = 5$ Hz, terminal methyl); MS, *m/e* 155 (parent − OMe), 144, 129, 112, 101, 85, 59, 57.

Nonelectrochemically Initiated Autoxidation. (Note ref 8). With a constant stream of molecular oxygen being passed into the solution, tetra-*n*-butylammonium hydroxide (2 mL, 0.54 mmol), dissolved in acetonitrile, was added via syringe pump over a 45-min period to a stirred solution of 100 mg (0.57 mmol) of methyl 4-nitro-2-methylpentanoate dissolved in 10 mL of acetonitrile. Analytical GC analysis indicated that the reaction rate plateaued after ca. 6 h; therefore, an additional 0.5 equiv of $(n\text{-Bu})_4NOH/CH_3CN$ was added at that time and again after a total of a 7-h reaction time. Workup was initiated after 10.5 h and proceeded in a fashion that was identical with that described above for the superoxide-initiated autoxidations. Purification via silica gel chromatography afforded a 95% mass balance consisting of 67% of the desired product and 33% starting material.

Determination of the Nitrogen-Containing Byproduct of the Autoxidation. Following the superoxide-initiated autoxidation procedure outlined above, 1.98 g (22.2 mmol) of 2-nitropropane was converted to acetone, which was identified after distillation and derivatization as the 2,4-dinitrophenylhydrazone. The aqueous layer that was obtained after washing the pot residue with water was subjected to the standard qualitative analysis sequence detailed by Margolis for the detection of nitrite and nitrate ions.[9] Positive tests for nitrite, but not nitrate ion, were observed. Each analysis was run in triplicate and each test solution was compared with that obtained from solutions containing known amounts of either nitrite or nitrate ion.

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Registry No. O_2^-, 11062-77-4; azobenzene radical anion, 34516-68-2; nitrocyclohexane, 1122-60-7; cyclohexanone, 108-94-1; cyclohexanone dinitrophenylhydrazone, 1589-62-4; 5-nitro-2-hexanone, 35223-72-4; 2,5-hexanedione, 110-13-4; 5-nitro-2-hexanone ethylene ketal, 84602-25-5; 2,5-hexanedione ethylene ketal, 33528-35-7; methyl 2-methyl-4-nitropentanoate, 16507-04-3; methyl 2-methyl-4-oxopentanoate, 32811-25-9; methyl 4-nitro-3-phenylpentanoate, 84602-26-6; methyl 4-oxo-3-phenylpentanoate, 25359-49-3; nitroethane, 79-24-3; methyl methacrylate, 80-62-6; methyl crotonate, 18707-60-3; methyl 3-methyl-4-oxopentanoate, 25234-83-7; ethyl cinnamate, 103-36-6; ethyl 4-oxo-3-phenylpentanoate, 63795-90-4; 2-cyclopentenone, 930-30-3; 3-acetylcyclopentanone, 84602-27-7; isophorone, 78-59-1; pulegone, 89-82-7; 1-nitropentane, 628-05-7; methyl 2-methyl-4-oxooctanoate, 16493-44-0.

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(14) Bel'skii, I. F.; Shostakovskii, V. M.; Vol'Nova, Z. K.; Ishchenko, S. I.; Glukhovtsev, V. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 420–422.

(15) **Note Added in Proof**: Recently, Kornblum and co-workers have reported the use of potassium permanganate to convert nitro paraffin salts to aldehydes and ketones in high yield. See: Kornblum, N.; Erickson, A. S.; Kelly, W. J.; Henggeler, B. *J. Org. Chem.* **1982**, *47*, 4534–4538.