Electrogenerated Bases. VI. Reaction of Electrogenerated Superoxide with Some Carbon Acids. II.*

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Electrogenerated superoxide and molecular oxygen were allowed to react sequentially with a number of esters, nitriles, N,N-dialkylamides, sulfones, and aliphatic nitro compounds. The α-methyl groups in these compounds bore aliphatic and/or aromatic substituents. When the electron-withdrawing group (EWG) of these carbon acids could be displaced intact (nitrile 2, ArSO₂
₄, nitro) good to excellent yields of the corresponding carbonyl compounds could be obtained. The efficiency of the transformation depended upon the nature of the substituents: α,α-diphenyl (e.g., 2a) > α-methyl-α-phenyl (2b) > α,α-dimethyl. By conducting the electrolysis in the presence of acetic anhydride it was shown that the known conversion of phenylacetonitrile (2d) to benzoic acid did indeed proceed via benzaldehyde. When the EWG itself could be cleaved (esters 1, N,N-dialkyl-amides 3), this methodology produced α-hydroxylated compounds and the products resulting from fragmentation of the EWG and also from its complete displacement. The effects of the α-substituents were similar to those above.

Superoxide may function as a radical, an electron-transfer agent, a nucleophile, or a base. Examples of these behaviors are cited in Ref. 2. As part of a broader program in synthetic utilization of electrogenerated bases (EGB), we have here focused upon the behavior of carbon acids RH (electroinactivate in these systems) of adequately low pKₐ toward a stream of O₂ which

\[ \text{X} \]
\[ \text{H-C-Z} \]
\[ \text{Y} \]

X=H, alkyl, aryl, RO ArO, etc.
Y=Z or H, alkyl, aryl
Z=electron-withdrawing group

1a, X=H, Y=CH₃, Z=COOEt
1b, X=H, Y=C₆H₅, Z=COOEt
1c, X=Y=CH₃, Z=COOCH₃
1d, X=Y=C₆H₅, Z=COOCH₃
1e, X=H, Y=Me₂CH, Z=COOEt
1f, X=H, Y=EtOCOCH₂, Z=COOEt
1g, X=H, Y=EtOCH₂CH₂CH₂, Z=COOEt

It was anticipated² that the nature of the reaction sequence would depend upon the identity of Y, particularly whether it could be displaced intact (e.g., −NO₂) or in part (e.g., COOR) or not at all, upon the pKₐ of I, and upon steric and electronic effects inherent in X and Y. For a series of malonate esters (1, Y=Z=COOR)

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reactions depended upon structure; products representing either oxygenation of the intact molecule or oxygenation and cleavage were obtained. A monoalkyl acetate was usually only saponified in a well preceded reaction while an alkyl monophenyl acetate was oxygenated and cleaved. In all cases when X or Y in I was H difficulties arose.

We report here an extension of this methodology to selected additional esters, nitriles, N,N-dialkylamides, sulfones, and nitro compounds. New, convenient and useful syntheses of oxygenated species have emerged from this work; elucidation of mechanisms remains to be accomplished.

Esters. The behavior of alkyl mono-substituted acetates (Ia, X=H, Y=CH₃, Z=COOEt; Ib, X=H, Y=C₆H₅, Z=COOEt) has been reported. It must be added that Ia gave erratic results with O₂₋+O₂, sometimes showing no reaction and sometimes yielding a mixture of ethyl lactate (15%) and lactic acid (35%); the latter obviously is a product of α-hydroxylation and saponification. We have not yet resolved these discrepancies.

Alkyl di-substituted acetate (Ic, X=Y=CH₃, Z=COOCH₂; Id, X=Y=C₆H₅, Z=COOCH₂) gave more promising yields of α-hydroxylated compounds: Ic was hydroxylated and saponified to 40% of 2-hydroxy-2-methylpropionic acid, Id was hydroxylated and cleaved to methyl 2,2-diphenyl-2-hydroxyacetate (45%) and benzophenone (10%), respectively. Cleavage when α-phenyl-groups are present seems to be usual. Mono-esters which are dialkylated at positions remote from the α-position (e.g., Ie, X=H, Y=Me₂CH, Z=COOEt) gave only, inseparable mixtures of compounds.

Unlike gem-diesters (malonates) but like acetates, α,ω-diesters in which the COOR groups were separated by n(CH₂) reacted poorly: diethyl succinate (If, X=H, Y=EtOOCCH₂, Z=COOEt) yielded only 4% of dl-tartaric acid while diethy1 adipate (Il, X=H, Y=EtOCH₂CH₂CH₂, Z=COOEt) did not react at all.

The new data for esters are summarized in Table 1. The limitations of O₂₋ as an EGB are pointed out by contrasting our results with those obtained when methyl esters were converted at −75 °C to their enolate anions by the very strong base lithium N-cyclohexyl-N-isopropylamide and then oxygenated: good yields (43–69%) of α-hydroperoxyl esters resulted. Depending upon structure, the latter decomposed thermally to mixtures of products including the α-hydroxy esters.

Nitriles. To the best of our knowledge there is only one report in which O₂₋+O₂ have been allowed to react with nitriles: phenylacetonitrile

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**Table 1. Behavior of selected esters toward O₂₋+O₂.**

<table>
<thead>
<tr>
<th>Ester (No.)</th>
<th>Products</th>
<th>Isolated yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCH₂COOEt (Ia)</td>
<td>MeCH(OH)COOEt</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>MeCH(OH)COOH</td>
<td>35</td>
</tr>
<tr>
<td>Me₂CHCOOMe (Ic)</td>
<td>Me₂C(OH)COOH (MW 104)</td>
<td>40</td>
</tr>
<tr>
<td>Ph₂CHCOOMe (Id)</td>
<td>Ph₂C(OH)COOMe (MW 242)</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Ph₂CO (MW 182)</td>
<td>10</td>
</tr>
<tr>
<td>Me₂CH COOMe (Ie)</td>
<td>complex mixture</td>
<td>-</td>
</tr>
<tr>
<td>(CH₂COOEt)₂ (If)</td>
<td>CH₂COOEt</td>
<td>dl-</td>
</tr>
<tr>
<td></td>
<td>HOCHCOOEt</td>
<td>meso-</td>
</tr>
<tr>
<td>(CH₂CH₂COOEt)₂ (Il)</td>
<td>no reaction</td>
<td>-</td>
</tr>
</tbody>
</table>

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*Divided cell, Hg cathode, Pt anode. Dry DMF+0.1 M Et₄NBr. Ester and stream of O₂ in catholyte, cyclohexene in anolyte. T=20 °C. Cathode voltage -0.9 to -1.0 vs. SCE. 1 F/mol was passed.*

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was converted to benzoic acid, presumably via PhCHO. Superoxide is capable of deprotonating CH₂CN but in the work done the (CH₂CN)⁻ was not exposed to oxygen but rather trapped by PhCHO. Anions of sec-nitriles were (a) prepared at −78 °C via lithium diisopropylamide (LDA); (b) the anions reacted with O₂ to yield (c) after quenching with aqueous acid or acetyl chloride, hydroperoxide derivatives which were (d) reduced by Sn(II) to cyanhydrins; the latter on treatment (e) with alkali provided the final product ketones in excellent yields. Aromatic nitriles are inert toward O₂⁻.

\[
\begin{align*}
X \\
H - C - CN \\
Y
\end{align*}
\]

 \[2a, X = Y = \text{Ph}\]  \[2b, X = \text{Ph}, Y = \text{Me}\]  \[2c, X = Y = \text{Me}\]  \[2d, X = \text{H}, Y = \text{Ph}\]  \[2e, X = \text{H}, Y = \text{Me}\]  \[2f, X = Y = \text{H}\]

Electroreduction of O₂ in the presence of selected nitriles 2 under our “standard” conditions (see Experimental) provides a convenient “one-pot” method for oxidative decyanation. The data are gathered in Table 2.

Good yields of ketones were obtained from sec-nitriles containing at least one aromatic substituent (2a, 2b). Isobutyronitrile (2c) gave only 20 % of acetone. Due to the anticipated instability in this system of aldehyde intermediates produced from primary nitriles, electrolyses in these cases were carried out both in the absence and in the presence of acetic anhydride. Primary nitriles (2d, 2e) were converted to carboxylic acid in the absence of Ac₂O and to the aldehyde diacetates in its presence. Acetonitrile (2f) behaved similarly. In all cases conversions were poor when only aliphatic substituents or H were at the α-position; the inadequately low pKₐ of these derivatives toward reaction with O₂⁻ is of greater importance than the small steric effects of the Ph groups in 2a–2b, and 2d.

In the case of the nitriles 2 and of the classes of compounds discussed below it was of interest to attempt to determine the fate of the leaving group (Z in 1). For this purpose the products of

Table 2. Reaction of O₂⁻ + O₂ with selected nitriles.¹

<table>
<thead>
<tr>
<th>Nitrile (No.)</th>
<th>F mol</th>
<th>Products</th>
<th>Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂CHCN (2a)</td>
<td>0.8</td>
<td>Ph₂CO</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MeNCO and trimer b</td>
<td>75</td>
</tr>
<tr>
<td>PhCH(CH₃)CN (2b)</td>
<td>1.0</td>
<td>PhCOCH₃</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2b</td>
<td>20</td>
</tr>
<tr>
<td>Me₂CHCN (2c)</td>
<td>1.0</td>
<td>(CH₃)₂CO</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2c</td>
<td>74</td>
</tr>
<tr>
<td>PhCH₂CN (2d)</td>
<td>1.8</td>
<td>PhCOOH</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>1.8 c</td>
<td>PhCOOH</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PhCH(OAc)₂</td>
<td>54</td>
</tr>
<tr>
<td>CH₂CH₂CN (2e)</td>
<td>1.0</td>
<td>CH₃COOH</td>
<td>15 d</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>CH₃COOH</td>
<td>5 d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃CH(OAc)₂</td>
<td>18 d</td>
</tr>
<tr>
<td>CH₃CN (2f)</td>
<td>0.22</td>
<td>HCOOH</td>
<td>0.18 c f</td>
</tr>
<tr>
<td></td>
<td>0.22 c</td>
<td>HCOOH</td>
<td>0.04 c f</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃(OAc)₂</td>
<td>0.14 c f</td>
</tr>
</tbody>
</table>

¹ H-cell, Hg cathode, Pt anode. DMF/Bu₄NBr. O₂ stream, −1.0 V vs. SCE. 4–5 mmol of substrate. b After addition of MeI to the catholyte. See text. c Ac₂O present. d 75–80 % of 2e recovered. e mol/F. f 70–73 % of 2f was recovered.

the reaction of 2a which had given the cleanest conversion to ketone were carefully examined. Addition of methyl iodide at the end of the electrolysis to react with *in situ* R₂N⁺CN⁻ or R₂N⁺CNO⁻ yielded only MeNCO and its trimer, trimethyl isocyanurate. No conclusions, however, can be drawn about the initial expelled fragment since control experiments showed that in the absence of 2, the CN⁻ of Bu₄N-CN is inert to O₂ but is oxidized to the same end products by O₂⁻.

N,N-Dialkylamides. Both benzamide and N-(α-phenylethyl)acetamide have been reported to be inert toward O₂⁻. However, when N-substituted amides were first converted to their anions by LDA at 0 or −78 °C and then oxygenated, they yielded α-hydroperoxides which were reduced by aqueous sodium sulfite to give excellent overall yields of α-hydroxy-N-substituted amides. No C–C cleavage products were found nor presumably were C–N cleavage products. The sequence succeeded even with RCH₂CONMe₂.

One of the mechanisms proposed for the hydrolysis of esters by superoxide involved initial nucleophilic attack upon the carbonyl of the ester group with expulsion of −OR. It was of interest to us, *inter alia*, to determine whether a similar cleavage (with the less likely expulsion of −NR₂) would occur with N,N-disubstituted amides.

As was the case with esters, the amides 3, depending upon structure,

\[
\text{X} \\
\text{HC-CONEt₂} \\
\text{Y}
\]

\[
3a, \ X=Y=\text{Ph} \\
3b, \ X=\text{Ph}, \ Y=\text{Me} \\
3c, \ X=Y=\text{Me} \\
3d, \ X=\text{Ph}, \ Y=\text{H}
\]

yielded α-hydroxylated and cleavage products or did not react at all (3c in Table 3). The similarity in behavior of 3d and 1d (Table 1) is striking; the fragmentation products (Et₂NH and CO₂) were collected and identified. A possible sequence of reactions, similar to those proposed previously for the cleavage of ethyl phenylacetate, is

\[
\text{Ph₂CHCONEt₂} \xrightarrow{O₂⁻} \text{Ph₂CHCONEt₂} \xrightarrow{O₂} \text{Ph₂C-CONI} \\
\xrightarrow{\text{O–O–}} \\
\xrightarrow{\text{H⁺}} \xrightarrow{\text{O–O–}} \xrightarrow{\text{−CO₂}} \xrightarrow{\text{H⁺}} \xrightarrow{\text{HNEt₂}} \text{Ph₂CO}
\]

Of potentially great synthetic importance is the report that α-hydroperoxides of esters, amides, ketones and nitriles epoxidize a number of

| Table 3. Reaction of O₂⁻ + O₂ with selected N,N-diethylamides.³ |
|--------------------|---------|--------------------|-----|
| Amide (No.)        | F mol   | Products            | Yields (%) |
| Ph₂CHCONEt₂ (3a)   | 1.5     | Ph₂CO               | 54  |
|                    |         | Ph₂C(OH)CONEt₂      | 40  |
|                    |         | CO₂                 | 30  |
|                    |         | Et₂NH               | 21  |
| Ph(CH₃)CHCONEt₂ (3b)| 1.2     | PhCOCH₃             | trace |
|                    |         | Ph(CH₃) C(OH) CONEt₂| 53  |
| Me₂ CHCONEt₂ (3c)  | 1.5     | no reaction         | –   |
|                    |         | 3c                  | 80  |
| PhCH₂CONEt₂ (3d)   | 1.2     | PhCOOH              | 5   |
|                    |         | PhCH(OH)CONEt₂      | 30  |
|                    |         | unknown              | –   |

³ H-cell, Hg cathode, Pt anode. DMF/Bu₄NBr. 4.0 mmol substrate. O₂ stream; −1.0 V vs. SCE. ⁴ 30% of starting material was recovered.
olefins, albeit sometimes very slowly. The presumed hydroperoxide anion intermediates formed by the action of O$_2$^{-}+O$_2$ on the compounds discussed in our paper participate in several competitive followup reactions: transfer of oxygen to the parent carbanion, nucleophilic displacement of a leaving group, reduction to alcohol; their effectiveness as epoxidizing agents will require that means be found for suppressing all other available routes. Up to the present, very small yields (<5%) of epoxides have been obtained from styrene and stilbene, respectively, by including these olefins in electrolytic experiments with 3a. Styrene alone with O$_2$^{-} is reported to yield no oxygenated products.

Sulfones. Only two representatives of 4 were studied in order to augment the generality of the behaviour of 1 when Z is an intact leaving group.

\[
\begin{align*}
4a, \ X = Y = \text{Ph} \\
4b, \ X = \text{Me}, \ Y = \text{Ph}
\end{align*}
\]

4a, after passage of 2 F/mol, yielded 90% of benzophenone; 4b (1.5 F/mol) gave 25% of acetophenone. Addition of MeI to the catholyte after electrolysis in the presence of 4a produced 65% of methyl benzenesulfonate; the latter is also formed from sulfinate (as Bu$_3$N$^+$SO$_2$Ph$^-$) with O$_2$ alone or O$_2$+O$_2$^{-}. These results contrast with those reported above for 2a.

Nitro compounds. The very facile conversion by this methodology of a variety of sec-aliphatic nitro compounds, including those containing other functionalities such as keto-, ester, aryl to their corresponding ketones has been reported separately. Additional examples, incorporating new features, have now become available. Primary nitro compounds (I, X or Y=H, Z=NO$_2$), as do other active methylene compounds with $\alpha$-methylene rather than $\alpha$-methyl, reacted poorly. 1-Nitrononane after short electrolysis (0.62 F/mol) yielded 36% nonanal. Starting material (16%) was recovered but no carboxylic acid was found. Longer electrolysis (1 F/mol) yielded an unresolved mixture of products not containing acid. An attempt to intercept the intermediate aldehyde by reducing O$_2$ in the presence of 1-nitropentane and A$_2$O$_2$ was unsuccessful: 16% of pentanoic acid and 33% of starting material was obtained but no aldehyde diacetate. Nitrocycloolefin (e.g., 5, 6) were converted to the respective \(a,\beta\)-unsaturated ketones in good yield. Nitro compounds under basic conditions are known to form hydroxamic acids which decompose on hydrolysis to carboxylic acids.

**EXPERIMENTAL**

**Study of esters.** A conventional H-cell with a G5 sintered glass diaphragm was used. The cathode was a 20 cm$^2$ Hg pool, the anode a Pt foil. The potentiostat was manufactured by Ultraschalltechnik Co. of Halle (DDR) The $^1$H NMR spectra (in CDCl$_3$ with hexamethyldisilane or tetramethysilane as internal standards) were obtained using an 80 MHz instrument BS 847C of Tesla; the mass spectra employed a Varian Match 6. For thin layer chromatography (0.2 mm) DC Alufolien Kieselgel 60 (Merck) was used; for preparative chromatography (PC) 2 mm. Developing agents were benzene (B), ethyl acetate (E) and methanol (M).

The general electrolysis procedure was as follows. About 1–3 g of starting ester, 100 ml of dry DMF together with 10 g of activated neutral Al$_2$O$_3$ dried at 400 °C at 5 Torr for at least 5 h and 0.01 mol of Et$_4$NBr were charged into the catholyte. The anolyte contained solvent/supporting electrolyte and 5 ml of cyclohexene. A stream of dry O$_2$ was bubbled through the catholyte. Electrolysis at −0.9 to −1.0 V vs. SCE was stopped after passage of 1 F/mol. Workup followed one or more of these procedures: (A) The DMF was removed from the catholyte in vacuo; the residue was extracted repeatedly with ether; the ether extract was washed with water, dried and evaporated to remove solvent. (B) like (A) except that the water washes were re-extracted with ether+CHCl$_3$, the extracts washed with a minimum of water, dried and combined with the above extracts. (C) The DMF was removed under N$_2$. The residue at 0 to −5 °C was brought to pH 10 and taken to dryness. The new residue was dissolved in the minimum amount of H$_2$O, adjusted to pH 1 with dilute HCl, and extracted several times with CHCl$_3$.

The extracts were washed minimally with water, dried and the solvent evaporated. (D) The catholyte at 0 to −5 °C was added to 200 ml of 3.5 % HCl. Distillation under N2 to 155 °C yielded a distillate containing DMF, HCl/H2O and products. The distillate was brought to pH 10 with 1N NaOH and evaporated to dryness under N2. The residue was then treated as in (C).

Methyl isobutyrate (1c). 2.05 g of ester, after electrolysis, yielded 0.97 of crude product which after purification by PC using B:E:M in the ratio 1:2:1 yielded purified α-hydroxyisobutyric acid (RF 0.35−0.45). After sublimation at 49 °C the product had RF 0.39. The IR spectrum showed OH at 3450 cm−1 and >C=O at 1695 cm−1. The MS (70 eV) showed m/e (%): 104(3), 73(100), 59(82). 1H NMR (CDCl3): δ 2.72 (S, 3H, CH3), 2.82 (S, 3H, CH3) and 7.94 (S, 1H, OH). The product was identical with an authentic sample.

Methyl diphenylacetate (1d). Electrolysis of 2.26 g at −0.9 V was followed by workup (A) to yield 1.25 g of crude. Purification by PC using B:E of 10:1 yielded 1d (RF 0.23), methyl α-hydroxydiphenylacetate (RF 0.5) and benzophenone (RF 0.7). The purified hydroxy-extr (RF 0.52), a viscous yellow oil, was 45 % of the crude mixture. In the IR it showed absorption at 1725 cm−1 (C=O) and at 3450 cm−1 (OH). The 1H NMR (δ) showed a singlet for 3H of OCH3, a singlet at 4.11 (OH, exchangeable with D2O) and a multiplet for 10 aromatic H at 7.15−7.50. The MS (70 eV) gave m/e (%): 242(12), 184(23), 183(100), 165(7), 152(8), 106(20), 105(95), 78(12) and 77(16). The benzophenone, 10 % of the crude after further purification, had RF 0.68 and IR spectrum identical to that in the literature. The MS (12 eV) showed m/e (%): 182(100), 105(81), 77(66).

Diethyl succinate (1f). Electrolysis at −0.9 V and workup (B) gave 0.8 g crude product purified by PC using B:E:M at 1:2:1. About 4 % of dl- and meso-diethyl tartrate was obtained with IR spectrum identical to that reported.15

Study of the other carbon acids. Equipment. An H-cell with medium porosity sintered glass separator was used. The cathode chamber was provided with ports for gas inlet (glass frit), luggin capillary leading to an SCE, and removal of samples. The cathode was Hg (ca. 7.1 cm2) and the anode a Pt foil (6.25 cm2). Each compartment held ca. 60 ml. The potentiostat was a Wenking 70 HV1/90 and the digital coulometer model 640 supplied by the Electrosynthesis Co. Analytical gas chromatography employed the Hewlett Packard model 5830A equipped with the HP 18850 data system; the column used was 1/8 in. × 0.5 m. 6 % SE-30. 1H NMR spectra were taken on a Varian T-60 spectrometer (Me4Si as internal standard); IR spectra on a Perkin-Elmer 283, and mass spectra on a VG ZAB-2F. For preparative column chromatography there were used (a) a gravity glow silica gel column (Merck, silica 60, 70−230 or 230−280 mesh), (b) a Chromatotron (Harrison Research, Model 7924) with a 2 mm thick silica gel rotor (Merck, silica 60, PF-254) and (c) an Aerograph A-90P preparative GLC unit equipped with a 6 mm×1.5 m in 5 % SE-30 column whose temperature was 150 °C. For thin layer chromatographic analysis Aldrich phosphomolybdc acid and an UV handlamp were used.

Materials. Acetonitrile (Mallinckrodt, spectral grade) was purified only by passage through a column of Sigma neutral alumina before use; the same solvent from other sources was first distilled under N2 from P2O5 before the alumina treatment. Dimethylformamide was vacuum distilled first from calcium hydride then from anhydrous CuSO4. It was stirred over freshly activated 3Å molecular sieves and passed through a column of alumina directly before use. Tetrabutylammonium bromide (Southwestern Analytical Chemicals, electrometric grade) was used as received. Molecular oxygen (Linde, 99.3 %) was passed through a 2×30 cm tube containing Drierite and NaOH pellets and then through 10Å Molecular Sieves (Sigma) before it was admitted into the cell. The nitriles 2 were purchased from Aldrich and purified by distillation or recrystallization as appropriate. Bu4NCl in DMF was made by double decomposition of Bu4NCI (Aldrich) and NaCN (Mallinckrodt) in this solvent and used directly after removing the NaCl by filtration. The N,N-dialkylamides 3 were prepared from the acid chlorides and diethylamine in ether and purified by distillation under reduced pressure. Each showed only one component by GLC. The sulfones 4a and 4b were prepared according to the literature. IR, 1H NMR and MS data as well as melting points were in agreement with the structures indicated. Tetrabutylammonium benzenesulfonate was prepared by acidifying the sodium salt (Aldrich), extracting into ether, evaporating to dryness, neutralizing with 40 % Bu4NOH (Aldrich) and again concentrating and drying in vacuo. 1-Nitropentane 19 and 1-nitrononane 20 were prepared according to the literature as were 1-nitro-1-cyclohexene (5) and bicyclo[4.4.0]nitroura-Δ5,3-decene (6).21

General procedure. The oven-dried H-cell was charged under Ar with 60 ml of solvent and 0.2 M Bu4NBr in each compartment. The solutions were pre-electrolyzed at −1.2 or −1.9 V vs. SCE until the background current decayed to 10 and 1 mA, respectively. Cyclohexene (ca. 1 ml) was added to the anolyte to trap liberated bromine and ca. 4 mmol of substrate was added to the

catholyte. Oxygen was bubbled through the catholyte; the cathode potential was controlled at −1.0 V. The consumption of the starting material was monitored by periodic TLC or GLC analysis. The workup procedure depended on the solvent that had been used: (a) when it was DMF the catholyte was poured into 60 ml of ice-water, the solution extracted with 5×100 ml of ether, the ether extracts washed with water, dried over MgSO₄, filtered and taken to dryness; when it was CH₂CN, about 80 % of the solvent from the catholyte was removed using a rot-o-vap with water aspirator, ether was added, the combined solutions washed with water and brine, dried (MgSO₄), filtered, and concentrated in vacuo. Deviations from this general procedure, necessitated by the physical properties of the starting material or products, are noted below.

Diphenylacetanitrite (2a). The general procedure (DMF) was followed. The ether residue after workup was benzophenone identical with an authentic sample. In other experiments designed to identify the composition of the leaving fragment, the electrolyzed catholyte (pH 10) was brought to pH 8–9 by addition of HOAc. Argon was bubbled through the solution to displace excess O₂ and MeI was added. After one hour’s stirring GLC analysis (SE-30 column) showed the presence of a small quantity of methyl isocyanate. After addition of water to the catholyte, a white precipitate was formed which, after recovery by filtration and recrystallization from ether—methanol, was shown to be trimethyl isocyanurate, m.p. 176 °C, unchanged by admixture with an authentic specimen.

2-Phenylpropionitrile (2b). Electrolysis under the general conditions (DMF) yielded 72 % of acetophenone and 20 % of unchanged starting material which were separated by column chromatography (ethyl ether—pentane). Each component was identical to a respective authentic sample.

Isobutylnitrile (2c). Since it was anticipated that the expected product, acetone, would be swept out of the cell by the O₂ stream, a trap containing aqueous 2,4-dinitrophenyldiazine sulfate was attached to one of the ports of the cathodic chamber. After the electrolysis, the derivative was found in the trap and no acetone, as judged by the same test, remained in the catholyte. Aqueous workup of the latter yielded the amount of starting material indicated (Table 2).

Phenylacetanitrite (2d). The starting material (3 mmol) was entirely consumed after 1.8 F/mol had been passed according to the general procedure (DMF). The workup procedure depended upon whether or not AC₂O (3 mmol) had also been added to the catholyte. In the absence of the anhydride the electrolyzed catholyte was brought to pH 3 by dilute HCl and extracted with several portions of ether. The ether extracts were washed, dried over MgSO₄, filtered, and evaporated to dryness yielding authenticated PhCOOH. When AC₂O had been included in the catholyte, the latter was diluted with cold water and directly extracted with ether. From the extract authenticated benzaldehyde diacetate was isolated. The catholyte was then acidified to pH 3, extracted with ether, etc. to recover PhCOOH.

Propionitrile (2e) and acetonitrile (2f). In each case, a Dry Ice—acetone cold finger was attached to the cathode chamber. The results given in Table 2 are typical of many experiments in which the system DMF/n-Bu₄NBr was used. The ratio of AC₂O to substrate was varied from 0 to 10. Generally a current of 85–110 mA was passed until 2000–2500 coulombs had been used. Products and unchanged starting materials were determined by GLC.

Tetraphenylammonium cyanide. The DMF solution of this cyanide as prepared above was charged to the cathode compartment of the cell. Bu₄NBr was added and O₂ was bubbled through for 2 h. A sample was removed, treated with MeI and then examined by GLC. MeCN but no MeNCNO or isocyannate was detected. The remainder of the catholyte was electrolyzed similarly to 2a; after displacement of O₂ the catholyte was treated with MeI, etc., yielding MeNCNO and its cyclic trimer.

N,N-Diethyl diphenylacetamide (3a). Two traps, one with saturated Ba(OH)₂, the other with 1 M HCl were attached to the cathode chamber. Standard electrolysis (DMF) with 4 mmol of 3a was carried out until the starting material had been consumed (1.5 F/mol). BaCO₃ and Et₂NH · HCl were recovered from the respective traps. Usual workup of the catholyte followed by column chromatography of the ether extracts on silica gel allowed separation of 2.2 mmol (54 %) of benzophenone and 1.6 mmol (40 %) of the α-hydroxylated N,N-diethylamide, m.p. 90 °C, identical with a sample prepared according to the literature.

N,N-Diethyl 2-phenylacetamide (3b). The procedure was similar to that used with 3a except that only 1.2 F/mol was arbitrarily used for the solution containing 4 mmol of 3b. The α-hydroxamide, m.p. 84 °C, was identical to the sample prepared according to Ref. 9.

N,N-Diethyl phenylacetamide (3d). Electrolysis was as in 3a, using 4 mmol of substrate and 1.8 F/mol. Workup of the acidified catholyte yielded the PhCOOH and the α-hydroxamide, m.p. 43 °C.
Diphenylmethyl phenylsulfone (4a). Standard electrolysis of a DMP solution containing 4 mmol of 4a was run until all the starting material had been consumed. The O₂ was displaced by Ar, Me₂ was added and the solution stirred for 1 h. Volatile materials were removed under reduced pressure. Addition of ether to the residue caused precipitation of n-Bu₂NBr which was removed by filtration. Column chromatography of the ether solution followed by elution with ether–pentane yielded 3.7 mmol (91 %) of benzophenone and 2.4 mmol (60 %) of methyl benzenesulfonate.

1-Phenylethyl phenyl sulfone (4b). 1 F/mol was used for the electrolysis of 1.6 mmol of 4b. The usual workup afforded 0.4 mmol (25 %) of acetophenone and unchanged starting material (0.91 mmol, 64 %).

Tetra(tributylammonium benzenesulfinate) dissolved in DMP + Bu₂NBr and treated with O₂ alone or O₂+O₂⁻ yielded after methylation methyl benzenesulfonate.

Nitro compound 5. The SSE was CH₃CN/n-Bu₂NBr. Electrolysis in the presence of 2.66 mmol of 5 at −1.1 V vs. SCE for 43 mins (1F/mol) yielded 73 % of cyclohexenone (7) as determined by GLC analysis on a 1.0 m 15 % SE-30 column using biphenyl as an internal standard and 46 % isolated yield (Kugelrohr distillation at 170 °C). ¹H NMR and IR spectra agreed with the expected. More by-products were obtained at a less negative cathode potential.

Nitro compound 6. The same SSE system as above was used. Electrolysis using 1.2 mmol of 6 at −1.0 V vs. SCE for 25 min (0.86 F/mol) yielded 59 % of the enone 8 and 20 % recovered 6. The compounds were separated by column chromatography using 15 % ether–Skelly Solve. The ¹H NMR and the IR spectra for 8 were satisfactory. Further, 8 was reduced completely with NaBH₄ in 1:1 ether–ethanol to the saturated alcohol identical by TLC, IR and GLC criteria with an authentic sample; the saturated alcohol on oxidation by the Jones Reagent yielded 2-decalone identical with a commerically available sample.

1-Nitrononane and 1-nitropentane. The same procedures as above were followed. The results have been presented in the Discussion.

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