# Cathodic Reduction of Acylated Vicinal Nitroalcohols

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Electrochemical elimination of vicinal groups is a well-known reaction; vic-dihalides,[1] diacetates,[2] hydroxysulfides,[3,4] hydroxysulfones,[5,6] and dinitro compounds have been reduced to unsaturated compounds. This communication is on the reductive elimination of acylated vicinal nitroalcohols; these compounds are readily available by acylation of the condensation products from an aldehyde with a nitroalkane.
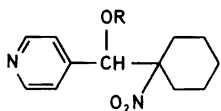


1a   R = H
1b   R = COCH$_3$
1c   R = COC$_6$H$_5$
1d   R = SO$_2$C$_6$H$_4$CH$_3$
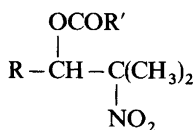


2a   R = 4-pyridyl                        R' = C$_6$H$_5$
2b   R = 2-pyridyl                        R' = C$_6$H$_5$
2c   R = 2-(1-methylimidazolyl)           R' = C$_6$H$_5$
2d   R = 4-nitrophenyl                    R' = C$_6$H$_5$
2e   R = C$_2$H$_5$                        R' = C$_6$H$_5$
2f   R = C$_2$H$_5$                        R' = CH$_3$
2g   R = C$_3$H$_7$                        R' = C$_6$H$_5$
2h   R = C$_4$H$_9$                        R' = C$_6$H$_5$
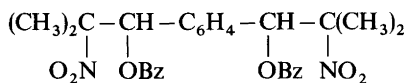


3   Bz = C$_6$H$_5$CO

*Results. Cyclic voltammetry (CV).* The cyclic voltammetry of *2f*, *2e* and *1c* in *N,N*-dimethylformamide (DMF) with tetrabutylammonium iodide as supporting electrolyte will be described (Table 1).

*Table 1.* CV peak potentials of some acylated vicinal nitroalcohols in DMF/TBAI; hanging mercury drop (HMD) electrode, reference electrode SCE, $v = 400$ mV s$^{-1}$.

| Substrate | $-E_1$/V | $-E_2$/V | $-E_3$/V |
|---|---|---|---|
| 1b | 1.60 | 2.40 | |
| 1c | 1.64 | 2.40 | |
| 1d | 1.52 | 2.39 | |
| 2a | 1.59 | 2.09 | 2.41 |
| 2b | 1.68 | 2.20 | 2.31 |
| 2c | 1.61 | 2.28 | |
| 2d | 1.22 | 1.88 | 2.25 |
| 2e | 1.75 | 2.34 | |
| 2f | 1.75 | | |
| 2g | 1.75 | 2.34 | |
| 2h | 1.76 | 2.34 | |
| 3 | 1.70 | 2.20 | 2.69 |

CV of *2f* gives one irreversible peak at low sweep rates ($v$); at higher $v$ an anodic peak appears; the peak separation between the cathodic peak and the corresponding anodic peak is about 100 mV at $v = 10$ V s$^{-1}$ and grows steadily to $> 200$ mV at $v > 800$ V s$^{-1}$. The relative current function ($i_p v^{-\frac{1}{2}}/i_p^\circ v^{-\frac{1}{2}}$, where $i_p^\circ$ is the peak current at high $v$) is 2 at $v = 0.4$ V s$^{-1}$ and diminishes to 1 at $v > 10$ V s$^{-1}$.

The first peak of *2e* behaves similarly to that of *2f*; *2e* shows, however, a second irreversible cathodic peak about 0.5 V more negative than the first one. The relative height of the second peak ($i_p(2)$) to that of the first peak ($i_p(1)$) changes from $i_p(2):i_p(1) = 1$ at low $v$ to about 2 at high $v$ ($v > 40$ V s$^{-1}$). The potential of the second wave is approximately where isopropyl benzoate (4) gives a peak which is reversible.

*1c* shows three cathodic peaks at low $v$; the two first peaks behave similarly to the peaks of *2e*, whereas the third one is reversible. When the height of the first peak diminishes with increasing $v$, the height of the third peak goes down and it disappears when the first peak is quasireversible.

In *2d* the first peak is due to the reversible reduction of the aromatic bonded nitro group.

*Preparative reductions.* Reduction of the substrates *1b − d* and *2a − d* at the potential of the first peak or at that of the second peak produced an alkene in fair to good yield (Table 2) in a two-electron reaction
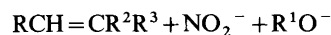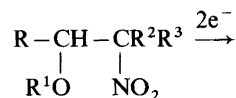
$$R - \underset{\underset{R^1O}{|}}{CH} - \underset{\underset{NO_2}{|}}{CR^2R^3} \xrightarrow{2e^-}$$

$$RCH = CR^2R^3 + NO_2^- + R^1O^-$$

*Table 2.* Yield (%) of products from an electrochemical reduction of some acylated vicinal nitroalcohols in DMF/TBAI. Potentials *vs.* SCE.

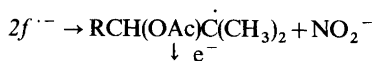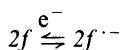| Substrate | $-E$/V | n/F mol$^{-1}$ | Yield | Products |
|---|---|---|---|---|
| *1a* | 1.70 | 1.0 | 12 | bicyclohexylidene (*7*) |
|  |  |  | 7 | nitrocyclohexane (*6*) |
|  |  |  | 66 | (NC$_5$H$_4$CHOH)$_2$ (*8*) |
| *1b* | 1.80 | 1.6 | 89 | 4-cyclohexylidenemethylpyridine (*9*) |
| *1c* | 1.80 | 1.8 | 70 | *9* |
| *1d* | 1.70 | 1.9 | 78 | *9* |
| *2a* | 1.80 | 1.7 | 68 | 2-methyl-1-(4-pyridyl)-1-propene (*10*) |
| *2b* | 1.80 | 1.8 | 66 | 2-methyl-1-(2-pyridyl)-1-propene (*11*) |
| *2c* | 1.80 | 1.8 | 22 | 1-(1-methyl-2-imidazolyl)-2-methylpropene (*12*) |
| *2d* | 1.40 | 4.9 | 11 | 4,4'-di(2-methyl-1-propenyl)azobenzene (*13*) |
| *2e* | 2.50 | 2.0 | $^a$ | 2-methyl-2-pentene (*14*) |
| *2f* | 2.50 | 1.6 | $^a$ | *14* |
| *2g* | 2.50 | 2.14 | $^a$ | 2-methyl-2-hexene (*15*) |
| *2h* | 2.50 | 2.30 | $^a$ | 2-methyl-2-heptene (*16*) |
| *3* | 1.80 | 3.5 | 47 | 1,4-di(2-methyl-1-propenyl)benzene (*17*) |

$^a$ Considerable loss of product during electrolysis and work-up.

The yield of olefin from *2e* − *h* was highest when the potential used during the reduction was 200 mV or more negative than the peak potential; reduction at the potential of the second peak produced also the olefin in good yield.

From the reduction of *1a* bicyclohexylidene, nitrocyclohexane and the pinacols from 4-pyridylaldehyd were isolated; the substrate suffered a retro-aldol condensation initiated by the electrogenerated base.

The aromatic bonded nitro group in *2d* is more easily reducible than the aliphatic bonded one, so the reduction of *2d* to an olefin was accompanied by a simultaneous reduction of the aromatic nitro group to an azo linkage. An olefin was formed even if the potential was held between the first and second peak.

*Discussion.* In *2f* the only electrophore is the nitro group; CV of *2f* is in accordance with an ECE or EC-Disp-1 mechanism, as the relative current function goes from 2 to 1 on increasing $v$ and an anodic peak appears at the same time. The reaction would thus be

$$2f \overset{\text{e}^-}{\rightleftharpoons} 2f^{\cdot -}$$

$$2f^{\cdot -} \rightarrow RCH(OAc)\overset{\cdot}{C}(CH_3)_2 + NO_2^-$$
$$\downarrow \text{e}^-$$
$$RCH(OAc)\overset{-}{C}(CH_3)_2$$
$$\downarrow$$
$$AcO^- + RCH = C(CH_3)_2$$

This explanation is not fully adequate for *2e*, as it has a second peak which does not disappear at high

*v.* This peak appears at a similar potential as the reversible peak of isopropyl benzoate (*4*). The peak is suggested to be caused by the benzoyl group in *2e*; this requires that the two electrophores, the nitro group and the benzoyl group, are sufficiently isolated from each other so the reduction of the nitro group does not significantly influence that of the benzoyl group; the two groups are separated by two $sp^3$-carbon atoms and one ether linkage.

The reduction of *4* is reversible, whereas the second peak of *2e* is irreversible. It seems plausible that further uptake of electrons to *2e* $^{\cdot -}$ or the carbanion from *2e* $^{\cdot -}$ would result in a fast cleavage with loss of benzoate.

The mechanism of the reduction of *2d* to the isolated product is different from that of *1c* and *2e*, as the initial electron uptake takes place at the 4-nitrophenyl group and the two nitro groups are isolated from each other by two $sp^3$-hybridized C-atoms. The formation of an olefin takes place even if the reduction is performed at a potential between the first and the second peak. A likely explanation is that *2d* $^{\cdot -}$ expels benzoate and that the resulting benzylic radical accepts an electron with loss of nitrite, followed by reduction of the nitro group to an azo group.

This is substantiated by the irreversibility of the first peak in CV (DMF/TBAI) of 4-nitrobenzyl benzoate (*5*) at low $v$ ($v$=40 mV s$^{-1}$); at higher $v$ ($v$ =0.8 V s$^{-1}$) the first peak of *5* is reversible. The irreversibility of *5* is probably due to a cleavage of *5* $^{\cdot -}$ with loss of benzoate.

*1a* undergoes a retro-aldol condensation and the nitrocyclohexane (*6*) is reduced to bicyclohexy-

lidene. The reaction has been suggested[7] to be a chain reaction involving homogeneous electron transfer from the nitrocyclohexane anion ($6^-$) to an acceptor, followed by coupling of $6 \cdot$ with $6^-$, loss of nitite, and reductive loss of a second nitrite.

*Experimental. Materials.* The nitroalcohols were prepared following known procedures[10,11] and acylated with the corresponding acyl chloride in cold pyridine. *1a*, m.p. 174−175 °C; *1b*, m.p. 138−139 °C; *1c*, m.p. 175−176 °C; *1d*, m.p. 125−127 °C; *2a*, m.p. 123−125 °C; *2b*, m.p. 84−85 °C. *2c*, m.p. 144−145 °C, *2d*, m.p. 128 °C; *2e*, oil, ¹H NMR (CDCl₃): δ 0.97 (3 H, t, 7 Hz), 1.63 (3 H, s), 1.70 (3 H, s), 1.45−1.98 (2 H, m), 5.63 (1 H, dd, 8 Hz, 6 Hz), 7.23−8.10 (5 H, m); *2f*, oil. ¹H NMR (CDCl₃): δ 0.93 (3 H, t, 7 Hz) 1.60 (3 H, s), 1.62 (3 H, s), 1.30−1.70 (2 H, m), 2.00 (3 H, s), 5.43 (1 H, dd, 8 Hz, 5 Hz); *2g*, oil, ¹H NMR (CDCl₃): δ 0.77−1.68 (7 H, m), 1.63 (3 H, s), 1.67 (3 H, s), 5.70 (1 H, def. d), 7.33−8.10 (5 H, m); *2h*, oil, ¹H NMR (CDCl₃): δ 0.87−1.70 (9 H, m), 1.62 (3 H, s), 1.67 (3 H, s), 5.67 (1 H, t, 6 Hz), 7.33−8.10 (5 H, m).

*General procedure for reduction.* The substrate (100−150 mg) was reduced at a stirred mercury electrode at the potential listed in Table 2 in 70 ml of DMF/0.1 M TBAI. When the reduction was completed (n-values listed in Table 2) the catholyte was poured into water (300 ml) and extracted with diethyl ether (3 × 150 ml); the pooled ether extracts were washed with water, dried (K₂CO₃), and evaporated *in vacuo*. The residue was purified by preparative TLC (alumina) using diethyl ether:light petroleum (1:1) as eluent.

The products from *2e−h* were isolated by passing a stream of nitrogen through the catholyte after the reduction and trapping the product (and some DMF) in a tube cooled in a dry-ice/acetone bath.

The following products were isolated: From *1b*, *1c*, and *1d:* 4-(cyclohexylidenemethyl)-pyridine, *9*, ¹H NMR (CDCl₃): δ 1.50−1.90 (6 H, m), 210−2.50 (4 H, m), 6.06 (1 H, s), 7.10 (2 H, br.s), 8.44 (2 H, br.s). From *2a:* 2-methyl-1-(4-pyridyl)-1-propene, *10*, ¹H NMR (CDCl₃): δ 1.86 (3 H, d, 2 Hz), 1.88 (3 H, d, 2 Hz), 6.15 (1 H, br.s), 7.02−7.12 (2 H, m), 8.43−8.53 (2 H, m). From *2b:* 2-methyl-1-(2-pyridyl)-1-propene, *11*, ¹H NMR (CDCl₃): δ 1.90 (3 H, d, 2 Hz), 2.03 (3 H, d, 1 Hz), 6.25 (1 H, m), 6.80−7.67 (3 H, m), 8.34−8.57 (1 H, m). From *2c:* 2-methyl-(1-methyl-2-imidazolyl)-1-propene, *12*, ¹H NMR (CDCl₃): δ 1.97 (3 H, d, 1 Hz), 2.15 (3 H, d, 1 Hz), 3.57 (3 H, s), 5.98 (1 H, m), 6.78 (1 H, d, 1 Hz), 7.05 (1 H, d, 1 Hz). From *2d:* 4,4′-di(2-methyl-1-propenyl)azobenzene, *13*, ¹H NMR (CDCl₃): δ 1.88 (12 H, br.s), 6.25 (2 H, m), 7.13−7.90 (8 H, m). From *2e* and *2f:* 2-methyl-2-pentene, *14*.[8] From *2g* 2-methyl-2-hexene, *15*, ¹H NMR (CDCl₃): δ 0.67−2.13 (7 H, m), 1.57 (3 H,

br.s), 1.65 (3 H, br.s), 5.07 (1 H, def.t). From *2h* 2-methyl-2-heptehe, *16*, ¹H NMR (CDCl₃): δ 0.67−2.07 (9 H, m), 1.58 (3 H, br.s), 1.67 (3 H, br.s), 5.08 (1 H, def. t).

From *3:* 1,4-Di(2-methyl-1-propenyl)-benzene, *17*, ¹H NMR (CDCl₃): δ 1.88 (12 H, br.s), 6.20 (2 H, m), 7.10 (4 H, s). From *1a:* Nitrocyclohexane, *6*, bicyclohexylidene, *7*, and the *d,l*-meso-mixture of 1,2-bis(4-pyridyl)-1,2-ethanediol, *8;* the latter mixture was separated into its components[9] by fractional crystallization from methanol.

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