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Formation of *N*-Acetyl-2,3-dihydroindoles by the Electrochemical Cleavage of the Carbon–Chlorine Bond in *N*-Allyl-2-chloroacetanilides

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Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday

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The electrochemically induced radical cyclization of *N*-allyl-2-chloroacetanilides to form *N*-acetyl-2,3-dihydroindoles has been demonstrated where the phenyl ring contains an electron withdrawing substituent such as cyano. Cyclization of *N*-allyl-2-chloroacetanilide was successful in the presence of (*E*)-stilbene as electron transfer agent yielding 1-acetyl-3-methyl-2,3-dihydroindole. Indirect electrochemical reduction of *N*-cinnamyl-2-chloroacetanilide leads mainly to cleavage of the cinnamyl group and only a low yield of *N*-acetyl-3-benzyl-2,3-dihydroindole was obtained.

Electrochemical reduction of aryl halides yields the radical anion as a short-lived intermediate which undergoes cleavage of the carbon–halogen bond to form an aryl radical and halide ion. Intramolecular cyclization of these electrochemically formed aryl radicals onto an adjacent benzene ring is a well established reaction.[1] The cathode material is often mercury but in some cases the reaction can be achieved as a constant current process at a steel cathode in acetonitrile.[2] The rates of some related intermolecular radical addition reactions have been determined in homogeneous solution.[3] The reaction between the phenyl radical and benzene has a rate constant of $4.5 \times 10^5\ M^{-1}\ s^{-1}$ while reaction between the same radical and styrene is faster with a rate constant of $1.1 \times 10^8\ M^{-1}\ s^{-1}$. These data suggest that the intramolecular reaction of electrochemically generated aryl radicals onto an adjacent alkene group should be achievable, in a similar manner to their reaction with an adjacent benzene ring. We demonstrate in particular the electrochemical conversion of **1a–c** into **2a–c**, respectively. Such electrochemical processes always have a competing side reaction in which the phenyl radical is further reduced at the electrode to form one of **3a–c** before it reacts with the adjacent group. This sequence of reactions is illustrated in Scheme 1. The series of substrates was chosen to illustrate how reaction conditions can be adapted to favour the cyclization route.

$ArX + e \rightleftharpoons ArX^{\cdot -}$	X = Halogen
$ArX^{\cdot -} \rightarrow Ar^{\cdot} + X^-$	Rate constant k_1
$Ar^{\cdot} \rightarrow$ cyclized radical	Rate constant k_2
$Ar^{\cdot} + e \rightarrow Ar^-$	

Scheme 1. Stages in the electrochemically induced radical cyclization of aryl halides.

Cyclization is successfully achieved when the time interval between electron addition and the carbon–halogen bond cleavage is sufficient to allow the radical anion intermediate to diffuse away from the electrode surface so that the σ-radical formed after bond cleavage cannot immediately accept a further electron from the cathode. The mean lifetime of this intermediate is equal to $1/k_1$. If this σ-aryl radical reacts only by cyclization onto the adjacent alkene bond then the mean lifetime is equal to $1/k_2$. During this period the σ-aryl radical may diffuse toward the electrode surface and undergo further reduction. Thus k_2 must be greater than k_1 for cyclization to be the predominant reaction.[4] In the final reaction stage, not shown in Scheme 1, the cyclised radical is

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either reduced to the carbanion, which is then protonated, or the radical abstracts hydrogen from the solvent.

Related radical cyclization processes have been demonstrated in the literature by reaction between aryl bromides and iodides with tributyltin hydride[5,6] or tris(trimethylsilyl)silane.[7] These are radical chain reactions in which halogen abstraction by a tin or a silicon radical generates the aryl radical, and aryl chlorides are unsatisfactory substrates. Our objective is to demonstrate an alternative electrochemical process which can utilise the cheaper aryl chloride substrates.

Results and discussion

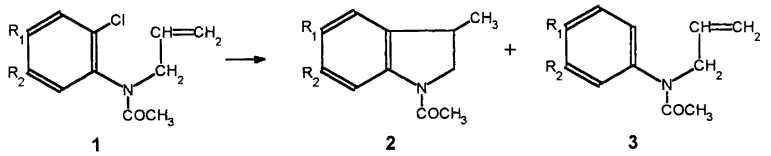
Cyclic voltammetry and preparative electrolyses. Compounds **1a–c** showed irreversible reduction waves during cyclic voltammetry at a voltage scan rate of $0.1\ V\ s^{-1}$. The peak potentials are given in the Experimental section. Compound **1c** is more difficult to reduce due to an absence of an electron-withdrawing substituent. Reduction of **1a** and **1b** at a mercury cathode led to the formation of the cyclised products **2a** and **2b**, respectively. In each case a minor product, **3a** or **3b**, was formed by replacement of the chloro substituent by a hydrogen atom. Direct reduction of **1c** at a mercury cathode, however, led only to the formation of **3c**; none of the cyclised product **2c** could be detected. These results are easily rationalised since the cleavage rates for the types of carbon–halogen bond under discussion are lowered by the presence of an electron-withdrawing substituent on the aromatic ring.[8] Thus k_1 for the radical anion derived from **1c** will be larger than the values for the radical anions derived from **1a,b**.

The cleavage rate for the chlorobenzene radical anion is known to be so fast that the two steps of electron addition and bond cleavage approach being concerted.[9] Thus, direct electrochemical cyclization of **1c** fails because for the series of reactions, k_2 is less than k_1. Conversion of **1c** into **2c** is the more potentially useful reaction and ideally we would like to achieve related reactions on substrates with electron donating substituents such as methoxy.

Utilization of an indirect electron transfer process was next examined to see whether this would promote the desired cyclization reaction using **1c** as the substrate. Here, an electron transfer agent yielding a relatively stable radical anion, and which is easier to reduce than the chlorobenzene substrate, is added to the reaction medium. Electrons are transferred preferentially from the electrode to this agent. Collision in solution between the so-formed radical anion and the substrate then leads to electron transfer followed by irreversible carbon–halogen bond cleavage. It is likely that cyclization of the aryl radical so formed will occur before a second electron can be transferred as the result of a further encounter with another radical anion. The reduction potentials of the electron transfer agent and the chloroarene substrate must be sufficiently close to give an effective rate for the intermolecular electron transfer step. Conversion of **1c** into **2c** was affected in an indirect process with either anthracene ($E^\circ = -1.92$ V vs. SCE)[10] or (*E*)-stilbene ($E^\circ = -2.17$ V vs. SCE)[11] as the electron transfer agent. (*E*)-Stilbene gave the desired product in better yields. This indirect electron transfer process is likely to be applicable to other substrates where no electron-withdrawing substituent is present.

Examination of the indirect electrochemical reduction of **4** illustrates a class of substrate where the cyclization step cannot be effected electrochemically in good yield due to a further competing side reaction. Compound **4** has been successfully cyclized by the tributyltin hydride method which involves atom transfer and not electron transfer reaction steps.[6] Electrochemical reduction of **4** was carried out using (*E*)-stilbene as the electron transfer agent. This gave a low yield of the desired product, **5**, the major product being 2-chloroacetanilide, **6**. The starting material has two isolated π-systems, each of which can accept the electron, and each system is associated with a frangible bond. 2-Chloroacetanilide is formed by cleavage of the carbon–nitrogen bond of the cinnamyl substituent to give a cinnamyl radical and the amide anion which is subsequently protonated. Compound **4** showed two irreversible reduction waves during cyclic voltammetry and these can be attributed to the reductive cleavage of the nitrogen–carbon bond of the cinnamyl group ($E_p = -2.28$ V vs. SCE) and reduction of 2-chloroacetanilide ($E_p = -2.62$ V vs. SCE).

Characterization of substrates and products. In general amides show extensive double bond character in the amide nitrogen–carbon bond.[12] This implies the existence of *Z*-and *E*-rotamers for **1a–c** where the amide carbonyl group is either adjacent to or remote from the phenyl ring. The ^1H NMR spectra of these compounds each show only one signal for the *N*-acetyl group which indicates that each has predominately only one rotamer present in solution. However, both the *E*- and the *Z*-

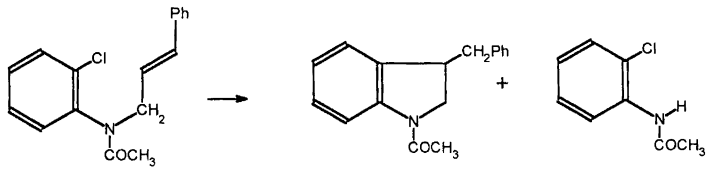


1 **2** **3**

a: $R_1 = CN$, $R_2 = H$

b: $R_1 = H$, $R_2 = CN$

c: $R_1 = R_2 = H$



4 5 6

rotamers are expected to undergo intramolecular radical cyclization following carbon–halogen bond cleavage.

The starting materials, **1a–c** and **4**, all show non-equivalence of the allylic methylene proton signals. This is because steric effects cause restricted rotation about the amide nitrogen–phenyl bond due to the *ortho*-halogen substituent. When bond rotation is slow on the NMR timescale, these allylic methylene protons are prochiral.[13] For some amides of related structure this restricted rotation gives rise to enantiomeric forms isolable at room temperature.[14] The reduction products **3a** and **3c**, where this halogen substituent has been replaced by hydrogen, cannot show this phenomenon since the phenyl group is symmetrically substituted about the nitrogen–phenyl bond. Compound **3b** is unsymmetrically substituted about the nitrogen–phenyl bond but non-equivalence of the allylic proton resonances could not be detected under our conditions.

Reaction products **2a–c** were isolated by chromatography and their identity was established by ^{1}H NMR spectroscopy. For each of these compounds the methylene protons are prochiral and the characteristic spectrum for the CH_2CHCH_3 group was identified. These *N*-acetyl-2,3-dihydroindoles all showed a low field resonance in the region $\delta = 8.2$–8.3 due to proton H-7 which is placed in the deshielding cone of the carbonyl group.[15]

Products **5** and **6** from reduction of **4** were isolated only as a mixture. Both are known compounds and their presence was established by examination of the ^{1}H NMR and MS of this mixture.

Experimental

Equipment, measurement procedures and electrochemical syntheses. ^{1}H NMR spectra were recorded on a Bruker Avance PPX 300 spectrometer at 300 MHz using tetramethylsilane as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz (derived from first-order analysis). Connectivities of protons were determined from decoupling experiments. Mass spectra were recorded using a VG instrument under conditions of electron impact.

Cyclic voltammetry was carried out in acetonitrile containing tetraethylammonium tetrafluoroborate (0.1 M) using instrumentation previously described.[16] The working electrode was an Hg drop hanging from a Pt electrode and a voltage scan rate of 0.1 V s^{-1} was used. Substrate concentrations were in the range 4–5 mM, the temperature was 23 °C. Anthracene was used as an external reference and the results were converted to the SCE scale by using the value, $E^\circ = -1.92$ V vs. SCE, for the reversible one-electron reduction.

Preparative electrochemical reduction was carried out at controlled current in an H-type cell with an Hg cathode ($A = 7$ cm^2) and a Pt anode, all maintained at room temperature. The cathode compartment required 15 ml of electrolyte [acetonitrile containing tetraethylammonium tetrafluoroborate (0.1 M)]. At the end of a run, the catholyte was collected and evaporated to a small volume under reduced pressure. The residue was partitioned between water and dichloromethane and the organic layer collected, washed with water and dried ($MgSO_4$), and the solvent removed.

Reagents. Acetonitrile, HPLC-grade distilled from calcium hydride, was used as the solvent in electrochemical reactions. Sodium hydride, obtained as a 60% suspension in oil, was washed with dry hexane before use. All other reagents were used as received.

3-Chloro-4-acetamidobenzoic acid. 2-Chloro-4-methylaniline (13.8 g) and acetic anhydride (40 ml) were stirred together at room temperature. After 40 min, when the exothermic reaction had subsided and a white solid precipitated, the reaction mixture was diluted with water (150 ml) to destroy the excess acetic anhydride. A precipitate of 2-chloro-4-methylacetanilide (17.5 g, 99%), m.p. 116 °C (lit.,[17] m.p. 113 °C) was collected. This compound (11.5 g) was oxidised with potassium permanganate according to the procedure of Schmelkes and Rubin[18] to yield 3-chloro-4-acetamidobenzoic acid (11.2 g, 84%), m.p. 236–238 °C (lit.,[18] m.p. 237–238 °C).

2-Chloro-4-cyanoacetanilide. Functional group conversion of carboxylic acid into nitrile was accomplished by the method of Imomoto *et al.*,[19] using the reaction between the ammonium salt and ethyl polyphosphate, prepared as described by Pollmann and Schamm.[20] 3-Chloro-4-acetamidobenzoic acid (6.5 g) was suspended in a mixture of chloroform (25 ml) and ethyl polyphosphate (18 g) contained in a three-necked flask fitted with an inlet for ammonia, generated by the slow evaporation of liquid ammonia, a stirrer and a reflux condenser. During the passage of ammonia, the mixture was kept in ice for 1 h, then at room temperature for 5 h after which it became very viscous. Monitoring by TLC (silica gel; eluting with chloroform–methanol 95:5) indicated the formation of an intermediate, R_f 0.2, assumed to be the carboxamide. The ammonia supply was disconnected, more ethyl polyphosphate (30 g) was added and

the mixture was refluxed with stirring from an oil bath at 85 °C. After 40 h, the carboxamide had largely been converted into the nitrile, R_f 0.7. The reaction mixture was stirred with sodium carbonate solution (25%, 450 ml) in ice for 1 h, then extracted with chloroform (3 × 200 ml). The combined organic extracts were washed with water, dried (Na_2SO_4) and the solvent removed. Crystallization of the residue from ethanol afforded 2-chloro-4-cyanoacetanilide (2.7 g, 45%) as colourless needles: m.p. 89–90 °C. IR (KBr): ν_{CN} 2226, ν_{CO} 1679 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.74 (s, NH), 8.09 (d, 1 H, H-6, J=8.6), 8.06 (1 H, H-3, J=1.0), 7.76 (dd, 1 H, H-5, J=8.6, 1.0), 2.15 (s, 3 H, $COCH_3$). MS: *m/z* (%) 196/194 (3.5/14.5) [M^+], 159 (5) [$M^+ - Cl$], 154/152 (32/100) [$M^+ - CH_2CO$], 43 (93) [CH_3CO^+]. Anal. calcd. for $C_9H_7ClN_2O$ (194.63): C, 55.54; H, 3.63; N; 14.40. Found: C, 55.19; H, 3.57; N; 13.96%.

N-*Allyl-2-chloro-4-cyanoacetanilide* (**1a**). To a stirred suspension of sodium hydride (0.72 g of 60%, 18 mM) in dry tetrahydrofuran (50 ml) was added dropwise a solution of 2-chloro-4-cyanoacetanilide (3.0 g, 15.4 mM) in dry tetrahydrofuran (100 ml) under nitrogen at −78 °C. The mixture became green and stirring was maintained for 2 h when a colourless precipitate formed. Allyl bromide (2.24 g, 18 mM) was then added and stirring was continued at −78 °C for 1 h and finally at room temperature for 18 h. The reaction mixture was then poured into water (100 ml) and extracted with ethyl acetate (3 × 60 ml). The combined extracts were washed with brine and dried ($MgSO_4$), and the solvent was removed. Chromatography on silica gel with dichloromethane as the eluent afforded *N*-allyl-2-chloro-4-cyanoacetanilide (2.2 g, 61%) as colourless needles: m.p. 89–90 °C. ^1H NMR ($CDCl_3$): δ 7.84 (d, 1 H, H-3, J=1.8), 7.64 (dd, 1 H, H-5, J=8.1, 1.8), 7.36 (d, 1 H, H-6, J=8.2), 5.84 (dddd, 1 H, $CH{=}CH_2$, J=17, 9.9, 7.5, 5.9), 5.04 (d, 1 H, $CH{=}CH_2$, J=17), 5.02 (d, 1 H, $CH{=}CH_2$, J=9.9), 4.69 (dd, 1 H, $CH_2CH{=}CH_2$, J=14.7, 5.9), 3.86 (dd, 1 H, CH_2CHCH_2, J=14.7, 7.5) 1.83 (s, 3 H, $COCH_3$). MS: *m/z* (%) 236/234 (4/11) [M^+], 199 (37) [$M^+ - Cl$], 194/192 (19/60) [$M^+ - CH_2CO$], 167/165 (9/30) [$M^+ - (CH_2CO + C_2H_3)$], 157 (55) [$M^+ - (Cl + CH_2CO)$], 43 (100) [CH_3CO^+]. Cyclic voltammetry: E_p = −1.82 V vs. SCE. Anal. calcd. for $C_{12}H_{11}ClN_2O$ (234.70): C, 61.41; H, 4.73; N, 11.94. Found: C, 61.56; H, 4.65; N, 11.87%.

2-Chloro-5-cyanoacetanilide. The corresponding amine was prepared[21] by reduction of 4-chloro-3-nitrobenzonitrile using stannous chloride, and purified by chromatography over a column of silica gel. Elution with dichloromethane afforded 3-amino-4-chlorobenzonitrile as pale yellow crystals m.p. 90–91 °C (lit.,[21] m.p. 92 °C). Reaction of the amine with acetic anhydride gave 2-chloro-5-cyanoacetanilide (98%) which crystallised from ethanol as colourless needles: m.p. 159–160 °C (lit.,[21] m.p. 158 °C). ^1H NMR ($CDCl_3$): δ 8.80 (d, 1 H, H-2, J=1.9), 7.70 (br s, 1 H, NH), 7.48 (d, 1 H, H-3, J=8.3), 7.32 (dd, 1 H, H-6, J=8.3, 1.9), 2.30 (s, 3 H, $COCH_3$).

N-*Allyl-2-chloro-5-cyanoacetanilide* (**1b**). 2-Chloro-5-cyanoacetanilide was reacted with sodium hydride and allyl bromide as described for the preparation of **1a**. The crude product was chromatographed on a column of silica gel and elution with hexane–ethyl acetate (2:1) afforded *N*-allyl-2-chloro-5-cyanoacetanilide (62%) which separated from ethanol as pale yellow crystals: m.p. 70–71 °C. ^1H NMR: δ 7.68 (d, 1 H, H-5/H-6, J=8.4), 7.64 (d, 1 H, H-6/H-5, J=8.4), 7.54 (s, 1 H, H-6), 5.84 (m, 1 H, $CH{=}CH_2$), 5.15 (dd, 1 H, $CH{=}CH_2$, J=10.2, 1.1), 5.05 (dd, 1 H, $CH{=}CH_2$, J=17.1, 1.1), 4.72 (dd, 1 H, $CH_2CH{=}CH_2$, J=15.0, 5.8), 3.80 (dd, 1 H, $CH_2CH{=}CH_2$, J=15.0, 7.7), 1.83 (s, 3 H, $COCH_3$). MS: *m/z* (%) 236/234 (1.5/5) [M^+], 199 (62) [$M^+ - Cl$], 194/192 (13/39) [$M^+ - CH_2CO$], 167/165 (9/19) [$M^+ - (CH_2CO + C_2H_3)$], 157 (61) [$M^+ - (Cl + CH_2CO)$], 43 (100) [CH_3CO^+]. Cyclic voltammetry: E_p = −1.78 V vs. SCE (broad peak due to the presence of a shoulder at E = −1.73 V vs. SCE). Anal. calcd. for $C_{12}H_{11}ClN_2O$ (234.70): C, 61.41; H, 4.73; N, 11.94. Found: C, 61.27; H, 4.82; N, 11.62%.

N-*Allyl-2-chloroacetanilide* (**1c**). 2-Chloroacetanilide (3.5 g, 20 mM) was added to a stirred suspension of sodium hydride (0.88 g of 60%, 22 mM) in dry tetrahydrofuran (100 ml) at −78 °C. Stirring was continued until a clear solution was obtained. Allyl bromide (2.4 g, 20 mM) was then added and stirring was continued at −78 °C for 45 min and then at room temperature overnight. The reaction mixture was poured into water (200 ml) and the product extracted with ethyl acetate. The combined organic extracts were washed with water and dried ($MgSO_4$), and the solvent was removed. *N*-Allyl-2-chloroacetanilide (2.70 g, 64%) distilled under reduced pressure as a colourless liquid: b.p. 130–134 °C at 0.1 mmHg. ^1H NMR ($CDCl_3$): δ 7.51 (d, 1 H, H-6, J=8.5), 7.34 (m, 2 H, H-5 + H-3), 7.22 (t, 1 H, H-4, J=8.6), 5.87 (m, 1 H, $CH{=}CH_2$), 5.08 (d, 1 H, $CH{=}CH_2$, J=10.5), 5.04 (ddd, 1 H, $CH{=}CH_2$, J=16.0), 4.70 (dd, 1 H, $CH_2CH{=}CH_2$, J=14.5, 6.0), 3.83 (dd, 1 H, $CH_2CH{=}CH_2$, J=14.5, 7.5). MS: *m/z* (%) 211/209 (6/10) [M^+], 174 (90) [$M^+ - Cl$], 169/167 (28/66) [$M^+ - CH_2CO$], 142/140 (25/70) [$M^+ - (CH_2CO + C_2H_3)$], 132 (73) [$M^+ - (Cl + CH_2CO)$], 43 (100) [CH_3CO^+]. Cyclic voltammetry: E_p = −2.49 V vs. SCE. Exact mass calcd. for $C_{11}H_{12}ClNO$ 209.0607. Found: 209.0606. Anal. calcd. for $C_{11}H_{12}ClNO$ (209.70): C, 63.02; H, 5.78; N, 6.68. Found: C, 62.85; H, 6.04; N, 6.62%.

N-*Cinnamyl-2-chloroacetanilide* (**4**). 2-Chloroacetanilide (3.5 g, 20 mM) was reacted with sodium hydride (0.88 g of 60%, 22 mM) in tetrahydrofuran (100 ml) and then cinnamyl bromide (3.92 g, 20 mM), as for the previous examples and the organic product was extracted with

ethyl acetate and dried ($MgSO_4$). The crude product was crystallised from aqueous ethanol to yield *N*-cinnamyl-2-chloroacetanilide (4.37 g, 76%) as pale yellow crystals: m.p. 88–90 °C. ^{1}H NMR ($CDCl_3$): δ 7.50 (dd, 1 H, H-6, J=8.8, 1.3), 7.34–7.18 (m, 3 H, aromatic), 6.37 (d, 1 H, CH_2CH=C<u>H</u>Ph, J=15), 6.29 (ddd, 1 H, $CH_2C\underline{H}$=CHPh, J=15, 7.0, 5.3), 4.81 (dd, 1 H, $C\underline{H}_2C\underline{H}$=CHPh, J=15, 5.3), 4.02 (dd, 1 H, $C\underline{H}_2CH$=CHPh, J=15, 7.0), 1.83 (s, 3 H, CH_3CO). Cyclic voltammetry: E_p = −2.28 and −2.62 V vs. SCE. Exact mass calcd. for $C_{17}H_{16}ClNO$ 285.0916. Found: 285.0917. Anal. calcd. for $C_{17}H_{16}ClNO$ (285.81): C, 71.45; H, 5.64; N, 4.90. Found: C, 71.63; H, 5.62; N, 4.97%.

Electrochemical reduction of N-*allyl-2-chloro-4-cyanoacetanilide* (**1a**). The compound (100 mg) was dissolved in the electrolyte (15 ml) and reduced at constant current (22 mA) for 40 min when the solution gradually became orange. The charge passed was 1.15 F. The organic products were separated by TLC on silica gel eluting with dichloromethane–ethyl acetate (98:2). The principal band, R_f 0.35, afforded 1-acetyl-5-cyano-3-methyl-2,3-dihydroindole, **2a** (25 mg), which was recrystallised from ethanol as colourless crystals: m.p. 175–177 °C. ^{1}H NMR ($CDCl_3$): δ 8.27 (d, 1 H, H-8, J=8.4), 7.52 (dd, 1 H, H-7, J=8.4, 1.5), 7.41 (s, 1 H, H-5), 4.28 (t, 1 H, $C\underline{H}_2CHCH_3$, J=9.9), 3.66 (dd, 1 H, $C\underline{H}_2CHCH_3$, J=9.9, 6.8), 3.54 (m, 1 H, $CH_2C\underline{H}CH_3$), 2.26 (s, 3 H, CH_3CO), 1.38 (d, 3 H, $CH_2CHC\underline{H}_3$, J=6.8): MS: *m/z* (%) 200 (43) [M^+], 158 (68) [$M^+ - CH_2CO$], 143 (100) [$M^+ - (CH_2CO + CH_3)$], 43 (83) [CH_3CO^+]. Exact mass calcd. for $C_{12}H_{12}N_2O$: 200.0949. Found: 200.0953. Anal. calcd. for $C_{12}H_{12}N_2O$ (200.26): C, 71.98; H, 6.04; N, 13.99. Found: C, 71.91; H, 5.95; N, 13.64%. *N*-Allyl-4-cyanoacetanilide, **3a** (5.3 mg) was isolated from the second band, R_f 0.16, as an oil: ^{1}H NMR ($CDCl_3$): 7.71 (d, 2 H, H-3+H-5, J=8.4), 7.31 (d, 2 H, H-2+H-6, J=8.4), 5.85 (ddt, 1 H, $CH_2C\underline{H}$=CH_2, J=17.0, 10.5, 6.1), 5.16 (d, 1 H, CH_2CH=C<u>H</u>$_2$, J=10.5), 5.09 (d, 1 H, CH_2CH=C<u>H</u>$_2$, J=17.0), 4.32 (d, 2 H, $C\underline{H}_2CH$=CH_2 J=6.1), 1.96, (s, 3 H, CH_3CO). MS: *m/z* (%) 200 (25) [M^+], 158 (100) [$M^+ - CH_2CO$], 157 (60) [$M^+ - (CH_2CO + H)$], 131 (50) [$M^+ - (CH_2CO + C_2H_3)$], 84 (30), 43 (55) [CH_3CO^+]. Exact mass: $C_{12}H_{12}N_2O$: 200.0949. Found: 200.0951.

Electrochemical reduction of N-*allyl-2-chloro-5-cyanoacetaldehyde* (**1b**). This compound (102 mg) was dissolved in the electrolyte (15 ml) and reduced at constant current (23 mA) for 40 min The charge passed was 1.12 F. The solution became red–brown in colour. The crude product was chromatographed on silica gel, eluting with dichloromethane–ethyl acetate (95:5) to give two products. 1-Acetyl-6-cyano-3-methyl-2,3-dihydroindole, **2b**, (28 mg) crystallized from ethanol as colourless needles: m.p. 113–116 °C. R_f 0.28. ^{1}H NMR ($CDCl_3$): δ 8.49 (s, 1 H, H-7), 7.33 (d, 1 H, H-5, J=11), 7.25 (d, 1 H, H-4, J=11), 4.27 (t, 1 H, $C\underline{H}_2CHCH_3$, J=9.5), 3.65 (dd, 1 H, $C\underline{H}_2CHCH_3$, J=9.8, 9.5), 3.56 (m, 1 H, $CH_2C\underline{H}CH_3$), 2.24 (s, 3 H, CH_3CO), 1.39 (d, 3 H, $CH_2CHC\underline{H}_3$). MS: *m/z* (%) 200 (35) [M^+], 158 (65) [$M^+ - CH_2CO$], 143 (100) [$M^+ - (CH_2CO + CH_3)$], 43 (69) [CH_3CO^+]. Exact mass calcd. for $C_{12}H_{12}N_2O$: 200.0955. Found: 200.0950. *N*-Allyl-3-cyanoacetanilide, **3b**, (12 mg) was isolated as an oil: R_f 0.15. ^{1}H NMR ($CDCl_3$): δ 7.66–7.43 (m, 4 H, aromatic), 5.85 (m, 1 H, $CH_2C\underline{H}$=CH_2), 5.28 (m, 2 H, CH_2CH=C<u>H</u>$_2$), 4.30 (d, 2 H, $C\underline{H}_2CH$=CH_2, J=6.1), 1.89 (s, 3 H, CH_3CO). MS: *m/z* (%) 200 (21) [M^+], 158 (95) [$M^+ - CH_2CO$], 157 (66) [$M^+ - (CH_2CO + H)$], 131 (50) [$M^+ - (CH_2CO + C_2H_3)$], 84 (54), 43 (68) [CH_3CO^+]. Exact mass calcd. for $C_{12}H_{12}N_2O$: 200.0950. Found: 200.0943.

Electrochemical reduction of N-*allyl-2-chloroacetanilide* (**1c**). This compound (100 mg) and (*E*)-stilbene (60 mg) were dissolved in the electrolyte (15 ml) and reduced at constant current (21 mA) for 62 min. The charge passed was 1.69 F. The organic products were separated by TLC on silica gel eluting with hexane–ethyl acetate (2:1) to give *N*-acetyl-3-methyl-2,3-dihydroindole, **2c**, (67 mg, 67%), which was recrystallised from aqueous ethanol as colourless needles: m.p. 78–80 °C (lit.,[6] m.p. 75–76 °C). R_f 0.24. ^{1}H NMR ($CDCl_3$): δ 8.23 (d, 1 H, H-7, J=7.9), 7.25–7.15 (m, 3 H, aromatic), 4.21 (t, 1 H, $C\underline{H}_2CHCH_3$, J=9.2), 3.58 (dd, $C\underline{H}_2CHCH_3$, J=9.2, 6.6), 3.52 (m, 1 H, $CH_2C\underline{H}CH_3$), 2.23 (s, 3 H, CH_3CO), 1.34 (d, 3 H, $CH_2CHC\underline{H}_3$, J=6.0). MS: *m/z* (%) 175 (45) [M^+], 133 (42) [$M^+ - CH_2CO$], 118 (100) [$M^+ - (CH_2CO + CH_3)$]. Exact mass calcd. for $C_{11}H_{13}NO$: 175.0997. Found: 175.1001.

Reduction of *N*-allyl-2-chloroacetanilide under the above conditions but in the absence of the mediator afforded *N*-allylacetanilide, **3c**, as the only product: R_f 0.31. ^{1}H NMR ($CDCl_3$): δ 7.42–7.35 (m, 3 H, aromatic), 7.18 (d, 2 H, H-2+H-6, J=8.5), 5.87 (m, 1 H, $CH_2C\underline{H}$=CH_2), 5.12 (d, 1 H, CH_2CH=C<u>H</u>$_2$, J=10.5), 5.08 (d, 1 H, CH_2CH=C<u>H</u>$_2$, J=17), 4.32 (d, 2 H, $C\underline{H}_2CH$=CH_2, J=6.2), 1.84 (s, 3 H, CH_3CO). MS: *m/z* (%) 175 (38) [M^+], 133 (100) [$M^+ - CH_2CO$], 132 (90) [$M^+ - (CH_2CO + H)$], 106 (75) [$M^+ - (CH_2CO + C_2H_3)$] 77 (55) [$C_6H_5^+$], 43 (63) [CH_3CO^+]. The identity was confirmed by comparison with spectral data from an authentic specimen.

Electrochemical reduction of N-*cinnamyl-2-chloroacetanilide* (**4**). The catholyte compartment contained this substrate (100 mg) and (*E*)-stilbene (60 mg) dissolved in the electrolyte (15 ml). Reduction at constant current (14 mA) was continued for 45 min for the passage of 1 F. The organic product was purified by TLC on silica gel, eluting with hexane–ethyl acetate (2:1) to yield a mixture of **5** and **6** in a ratio of 1:6 as a solid: m.p. 68–70 °C. R_f 0.49.

5: ^{1}H NMR ($CDCl_3$): δ 8.20 (d, 1 H, H-7, J=8.2), 7.4–7.0 (m, aromatic), 3.99 (dd, 1 H, $NC\underline{H}_2CHCH_2Ph$,

$J=12.0$, 6.9), 3.72 (d, 1 H, NCH_2CHCH_2Ph, $J=12.0$), 3.71 (m, 1 H, NCH_2CHCH_2Ph), 3.12 (dd, 1 H, NCH_2CHCH_2Ph, $J=13.8$, 5.1), 2.79 (dd, 1 H, NCH_2CHCH_2Ph, $J=13.8$, 8.6), 2.16 (s, 3 H, CH_3CO). MS: *m/z* (%) 251 (7) [M^+], 160 (7) [$M^+ - PhCH_2$], 118 (30) [$M^+ - (PhCH_2 + CH_2CO$], 91 (25) [$PhCH_2^+$]. Exact mass calcd. for $C_{17}H_{17}NO$: 251.1310. Found for **5**: 251.1304.

6 (and by comparison with an authentic sample): δ 8.35 (d, 1 H, H-6, $J=8.2$), 7.4–7.0 (m, 3 H, aromatic), 2.25 (s, 3 H, CH_3CO). MS: *m/z* (%) 171/169 (9/20) [M^+], 134 (35) [$M^+ - Cl$], 129/127 (40/100) [$M^+ - (Cl + CH_2CO)$].

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