

Electrochemical Reduction of *N*-(2,2,2-Trichloroethyl)acetamides

Maria Antonietta Casadei, Franco Micheletti Moracci, and Donatella Occhialini
*Istituto di Chimica Farmaceutica e Tossicologica, Università degli Studi 'La Sapienza', P. le Aldo Moro, 5,
 I-00185 Rome, Italy*

Achille Inesi*

Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia, Università degli Studi 'La Sapienza', Via del Castro Laurenziano, 7-00161 Rome, Italy

The electrochemical reduction, at a mercury cathode, of dimethylformamide solutions, containing Et_4NClO_4 as supporting electrolyte, of *N*-(2,2,2-trichloroethyl)acetamides (**1a–f**), with or without added water as proton source, has been investigated. In all cases, the nature and yield of the products from macroscale electrolyses as well as voltammetric data point to the formation of an intermediate carbanion, which undergoes β -elimination, or α -elimination, or acid–base reaction depending on the nature of the substituent on the carbon α to nitrogen and the medium. The formation of (**2a**) from the electrolysis of (**1a–b**) in the presence of H_2O has been ascribed to nucleophilic substitution of the first-formed dehalogenated product by dimethylamine. The latter arises from decomposition of the solvent promoted by ions released in the follow-up reactions of the carbanion.

The electrochemical reduction of *gem*-polyhalogeno derivatives has been investigated by several groups, yielding valuable results on the stereochemistry of the process¹ and the nature and reactivity of the intermediates. It has been found in several cases that carbanionic intermediates are formed from a two-electron reduction of a carbon–halogen bond. Depending on the nature of the 'parent' molecule and the medium, the carbanion can either undergo α -elimination, giving the corresponding carbene,² or behave as a base or a nucleophile towards added substrate and/or the depolarizer itself.³ If a good leaving group is present at the α position with respect to the polyhalogenated carbon, β -elimination, giving the corresponding unsaturated compound, can also be operative.⁴ According to the nature of the leaving group, either a 'concerted' (*E2*-like) mechanism or one 'somewhere between pure carbanion and concerted' has been invoked for this type of reaction.^{4b,c}

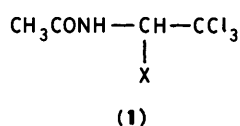
It follows that at present no *a priori* generalization can be made about the mechanism involved in electrochemical reduction of *gem*-polyhalogeno compounds, and further studies on this topic are necessary to clarify the picture.

In the course of previous work on the electrochemical behaviour of aliphatic halogenoamides,⁵ we incidentally investigated the electroreduction of *N*-(1-acetoxy-2,2,2-trichloroethyl)acetamide (**1a**), which gives *N*-(2,2-dichlorovinyl)acetamide (**3**), in almost quantitative yield. In order to explain the formation of (**3**), we postulated the intermediacy of a carbanion in the reduction (**1a**) \rightarrow (**3**), without any effort to test other possible mechanisms. However, further studies on this subject appear desirable on account of work by Merz,^{4c} who studied related compounds, 1-phenyl-2,2,2-trichloroethyl derivatives bearing a substituent at position 1.

We therefore studied the electrochemical reduction of *N*-(2,2,2-trichloroethyl)acetamides (**1a–f**).

Experimental

Electrochemical behaviour was investigated for solutions in *NN*-dimethylformamide (DMF), either anhydrous or containing 5% water as proton donor, containing tetraethylammonium perchlorate (TEAP) as supporting electrolyte, by means of cyclic voltammetry (sweep rate 0.2–500 V s^{-1}), coulometry, and



a; X = OCOCH_3

b; X = OCOPh

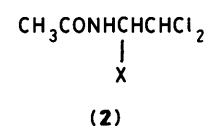
c; X = Cl

d; X = OC_2H_5

e; X = Ph

f; X = OH

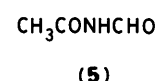
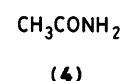
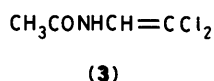
g; X = $\text{N}(\text{CH}_3)_2$



a; X = $\text{N}(\text{CH}_3)_2$

b; X = OC_2H_5

c; X = Ph



preparative controlled-potential electrolysis (c.p.e.). At the end of electrolyses, products were identified and characterized.

Voltammetric measurements were carried out at an Amel 498 sessile mercury drop electrode with an Amel 552 potentiostat equipped with an Amel 566 function generator and an Amel 563 multipurpose unit. The curves were displayed on an Amel 863 recorder assisted by a Nicolet 3091 digital oscilloscope. C.p.e. and coulometry were carried out at a mercury pool cathode with an Amel 552 potentiostat equipped with an Amel 721 integrator. The cells used for all these techniques have already been described.⁶ The reference electrode was of the calomel type described by Fujinaga;⁷ its potential was $-0.049 \text{ V versus s.c.e.}$, and did not change during the time of our experiments; all potential values are referred to this electrode. All the electrochemical measurements were performed at $20.0 \pm 0.1^\circ \text{C}$. DMF (Riedel–DeHaen spectranal) and TEAP (Fluka) were purified as previously described;⁶ the water content of DMF ($<0.01\%$) was ascertained by titration by the Karl Fischer method.

Column chromatography was carried out on Merck silica gel 70–230 mesh (150 g per 1 g substrate) using 95:5 CHCl_3 –

Me₂CO as eluant. M.p.s were taken with a Tottoli apparatus and are uncorrected. I.r. spectra were recorded for Nujol mulls with a Perkin-Elmer 177 grating spectrophotometer. N.m.r. spectra were recorded by means of a Varian EM-390 spectrometer and chemical shifts are relative to Me₄Si used as internal standard. Mass spectra were determined at 70 eV with a Hewlett-Packard 5980A low-resolution spectrometer equipped with a Hewlett-Packard 5934A data system.

All new compounds gave satisfactory elemental analytical data.

Compounds (**1a**–**f**) were prepared by standard procedures: (**1a**), m.p. 112–113 °C (lit.,⁵ 112–113 °C); (**1b**), m.p. 119–120 °C (lit.,⁸ 101–102 °C); (**1c**), m.p. 129–130 °C (lit.,⁹ 123–124 °C); (**1d**), m.p. 117–118 °C (lit.,¹⁰ 115–116 °C); (**1e**), m.p. 135–136 °C (lit.,¹¹ 142–143 °C); (**1f**), m.p. 164–166 °C (lit.,¹² 170 °C). For the preparation of compounds (**2a**–**c**) and (**3**) see c.p.e. of (**1a**–**e**). C.p.e. studies were carried out by stepwise addition of substrate, up to the total amount reported for the various runs, to DMF–0.1M-TEAP (50 ml), containing 5% water, when required. Electrolyses were stopped when the current had dropped from its initial value of 0.3 A to 10 mA. The voltammograms recorded at the end of the electrolyses showed the absence of any species reducible at the potential of the experiment and gave information on the nature and concentration of the species, reducible at potentials more negative, present in the solution. At the end of each electrolysis, the cathode was discharged, and the solvent removed at 40–50 °C under reduced pressure. The residue was extracted with Et₂O (5 × 50 ml), the insoluble solid was dissolved in H₂O, and extracted with CHCl₃ (5 × 30 ml). The combined organic layers were dried (Na₂SO₄) and the solvent was removed under reduced pressure. The residue was purified by column chromatography. Parameters concerning the various electrolyses and analytical data of the electrolysed solutions are given below.

Results and Discussion

Preparative Electrolyses.—**Reduction of (1a).** (a) In anhydrous DMF. This experiment has been already described:⁵ the only reduction product was *N*-(2,2-dichlorovinyl)acetamide (**3**) (94%).

(b) In DMF–H₂O (95:5). Compound (**1a**) (0.5 g) was reduced at –1.5 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.46 V. Column chromatography of the residue (0.38 g) from the work-up of the solution gave (**3**) (0.15 g, 48%), m.p. 84 °C (lit.,¹³ 86–87 °C) and (**2a**) (0.17 g, 44%), m.p. 93–94 °C (cyclohexane); $\bar{\nu}$ 3 270, 1 650, and 1 540 cm⁻¹; δ (CD₃COCD₃) 7.9–7.3 (1 H, br s, NH, exchanges with D₂O), 6.07 (1 H, d, CHCl₂, *J* 6 Hz), 5.00 (1 H, dd, CHNH, *J* 9 Hz, reduces to d with D₂O), 2.25 (6 H, s, NCH₃), and 2.00 (3 H, s, COCH₃); *m/z* 115 (*M*⁺ – CHCl₂).¹⁴

Reduction of (1b). (a) In anhydrous DMF. Compound (**1b**) (0.38 g) was reduced at –1.5 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.38 V. Potentiometric titration of the reduced solution shows the presence of 1.0 mol of Cl⁻ per mol of substrate. Column chromatography of the residue (0.25 g) from the work-up of the solution gave (**3**) (0.15 g, 80%).

(b) In DMF–H₂O (95:5). Compound (**1b**) (0.6 g) was reduced at –1.5 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.46 V. Column chromatography of the residue (0.48 g) from the work-up of the solution gave (**3**) (0.13 g, 44%) and (**2a**) (0.14 g, 36%).

Reduction of (1c) in anhydrous DMF. Compound (**1c**) (0.35 g) was reduced at –1.4 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.4 V. Column chromatography of the residue (0.28 g) from the work-up of the solution gave (**3**) (0.23 g, 96% yield).

The reduction of (**1c**) in aqueous DMF was not performed because in this solvent system the product undergoes decomposition.

Reduction of (1d). (a) In anhydrous DMF. Compound (**1d**) (0.98 g) was reduced at –1.8 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.47 V. Potentiometric titration of the reduced solution shows the presence of 2.3 mol of Cl⁻ per mol of substrate. Column chromatography of the residue (0.58 g) from the work-up of the solution gave (**2b**) (0.42 g, 50%), m.p. 53–54 °C (cyclohexane); $\bar{\nu}$ 3 250, 1 650, and 1 520 cm⁻¹; δ (CD₃COCD₃) 7.9–7.4 (1 H, br s, NH, exchanges with D₂O), 5.98 (1 H, d, CHCl₂, *J* 3 Hz), 5.50 (1 H, dd, CHNH, *J* 9 Hz, reduces to d with D₂O), 3.70 (2 H, m, OCH₂), 2.00 (3 H, s, COCH₃), and 1.17 (3 H, t, CH₃); *m/z* 154 (³⁵Cl*M*⁺ – Cl) and correct pattern for isotopic abundances.¹⁵

(b) In DMF–H₂O (95:5). Compound (**1d**) (0.2 g) was reduced at –1.8 V. The voltammograms recorded at the end of the electrolysis shows a reduction peak at *E* –2.40 V. Column chromatography of the residue (0.17 g) from the work-up of the solution gave (**2b**) (0.15 g, 88%).

Reduction of (1e). (a) In anhydrous DMF. Compound (**1e**) (1.0 g) was reduced at –1.8 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.44 V. Potentiometric titration of the reduced solution shows the presence of 2.2 mol of Cl⁻ per mol of substrate. Column chromatography of the residue (0.60 g) from the work-up of the solution gave (**2c**) (0.20 g, 23%), m.p. 121–124 °C (decomp.) (cyclohexane); $\bar{\nu}$ 3 270, 1 640, and 1 540 cm⁻¹; δ (CDCl₃) 7.40 (5 H, s, aromatic), 7.1–6.8 (1 H, br s, NH), 6.07 (1 H, d, CHCl₂, *J* 5 Hz), 5.63 (1 H, dd, CHNH, *J* 9 Hz), and 2.03 (3 H, s, CH₃); *m/z* 148 (*M*⁺ – CHCl₂).¹⁶

(b) In DMF–H₂O (95:5). Compound (**1e**) (0.63 g) was reduced at –1.8 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.41 V. Column chromatography of the residue (0.48 g) from the work-up of the solution gave (**2c**) (0.33 g, 60%).

Reduction of (1f). (a) In anhydrous DMF. Compound (**1f**) (0.58 g) was reduced at –1.8 V. The voltammogram recorded at the end of the electrolysis shows a reduction peak at *E* –2.53 V. Potentiometric titration of the reduced solution shows the presence of 1.1 mol of Cl⁻ per mol of substrate. After evaporation of the solvent, the residue was extracted with Et₂O (5 × 50 ml) and warm benzene (3 × 50 ml). The combined organic layers were dried (Na₂SO₄) and the solvent was removed under reduced pressure. N.m.r. analysis of the residue (0.16 g) shows the presence of CH₃CONH₂ (**4**) and CH₃CONHCHO (**5**) in the molar ratio 1:2. Column chromatography of the residue allowed the separation of the products: (**4**) (25 mg, 15%) was isolated using CH₂Cl₂–AcOEt (9:1) as eluant, whereas (**5**) (75 mg, 31%), m.p. 66–68 °C (lit.,¹⁷ 65–68 °C) was isolated using Me₂CO as eluant.

(b) In DMF–H₂O (95:5). Compound (**1f**) (0.70 g) was reduced at –1.8 V. The work-up of the reaction was as before. N.m.r. analysis of the residue (0.19 g) shows the presence of (**4**) and (**5**) in the molar ratio 1:1. Column chromatography of the residue gave (**4**) (0.06 g, 30%) and (**5**) (0.08 g, 27%).

The formation of (**2a**) can be explained as resulting from (i) preliminary conversion of (**1a** or **b**) into (**1g**), followed by reduction and protonation; (ii) nucleophilic substitution on (**2**; X = OCOR); or (iii) addition to (**3**), all involving (CH₃)₂NH arising from decomposition of DMF. In order to test these possibilities the following separate experiments were performed.

(a) **Reaction between (1b) and (CH₃)₂NH.** An excess of dimethylamine was slowly bubbled during 5 h into a solution of (**1b**) (0.31 g) in anhydrous DMF (50 ml), maintained with stirring at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in CH₂Cl₂, and extracted with aqueous NaHCO₃ and H₂O. The organic layer

Table 1. Peak potentials V versus s.c.e. (v 0.2 $V s^{-1}$) for (1a–g), (2a–c), and (3) ($1.0 \times 10^{-3} M$) in DMF–0.1M-TEAP, on a mercury cathode

Compound	E'_p	E''_p
(1a)	-1.55	-2.42
(1b)	-1.39	-2.38
(1c)	-1.32	-2.36
(1d)	-1.93	-2.37
(1e)	-1.86	-2.35
(1f)	-1.96	-2.53
(1g)	-1.65 ^a	-2.47 ^a
(2a)		-2.52
(2b)		-2.50
(2c)		-2.44
(3)		-2.34

^a In DMF + 5% H_2O .

was separated, dried (Na_2SO_4), and the solvent was removed under vacuum. Column chromatography of the residue (0.24 g) gave unchanged (1b) (0.08 g) and *N*-(1-dimethylamino-2,2,2-trichloroethyl)acetamide (1g) (0.14 g), m.p. 104–106 °C (cyclohexane); $\bar{\nu}$ 3 270, 1 660, and 1 540 cm^{-1} ; δ ($CDCl_3$) 6.6–6.2 (1 H, br s, NH), 5.38 (1 H, d, CH), 2.48 (6 H, s, NCH_3), and 2.13 (3 H, s, $COCH_3$); m/z 115 ($M^+ - CCl_3$).

(b) *Reaction between (3) and $(CH_3)_2NH$.* An excess of dimethylamine was slowly bubbled during 3 h into a solution of (3) (0.15 g) in anhydrous DMF (50 ml) maintained with stirring at room temperature. N.m.r. analysis of the residue from the evaporation of the solvent under vacuum showed the presence of unchanged (3) as the only product.

(c) *Formation of $(CH_3)_2NH$ by decomposition of DMF.* Experiments were performed by treating a solution of (1b) in DMF or DMF– H_2O (95:5), with or without added Hg, with sodium or tetra-alkylammonium benzoates. In no case was the formation of (1g) observed within the time usually employed for c.p.e. studies (0.5–2 h). However, (1g) was isolated in low yield (ca. 20%) after 20 h for reaction in anhydrous DMF and using equimolar amount of $PhCOO^-NEt_4^+$.

Voltammetry.—Two reduction peaks were found in the voltammetric curves of halogenoamides (1a–f) when recorded in DMF–0.1M-TEAP solutions. Table 1 shows the corresponding values of the peak potentials, as well as the reduction potentials of other halogenoamides, so that some features of the reduction of (1a–f) can be elucidated.

The usual voltammetric tests (I_p versus $v^{1/2}$) indicated that, for compounds (1a, b, d, and e), the first reduction peak is irreversible and diffusion-controlled, while the second shows a kinetically controlled reduction.

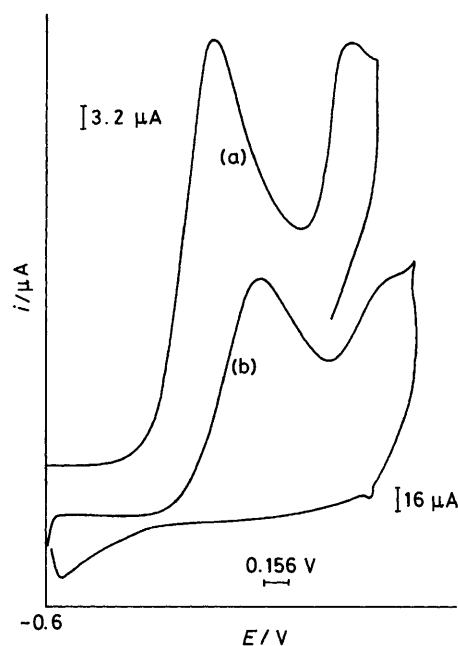
The electrochemical data and the analytical results obtained after exhaustive controlled-potential electrolyses, as well as the influence exerted on both by the presence of water, suggest the following observations on the reduction mechanism of halogenoamides (1a–f), and on the nature and reactivity of the intermediates.

(a) *Reduction of (1a and b).* The voltammetric curves show two reduction peaks [(1a) E'_p -1.55, E''_p -2.42 V; (1b) E'_p -1.39, E''_p -2.38 V; v 0.2 $V s^{-1}$]. The second reduction peak may be related to the formation of the unsaturated product (3) (E_p -2.34 V). If the voltammetric curve is recorded in the presence of H_2O , the value of the second peak (E_p -2.45 V) is affected by the presence of both the unsaturated product (3) and the hydrogenated product (2a) (see later).

When the preparative electrolyses are carried out in anhydrous DMF, the measured value of $n_{app} = 2$, the formation of the unsaturated product (3) in high yields [94% from (1a), 80% from (1b)], and the absence of hydrogenated products

Table 2. Voltammetric data for $1.0 \times 10^{-3} M$ solutions of (1b) in DMF–0.1M-TEAP at different values of the scan rate (v). The potential of the first peak and the currents of the first and second peaks are reported both in the absence and in the presence of H_2O (5%).

$v/V s^{-1}$	E'_p/V	$E'_p(H_2O)/V$	$i'_p/\mu A$	$i'_p(H_2O)/\mu A$	$i''_p/\mu A$	$i''_p(H_2O)/\mu A$
5	-1.61	-1.58	30.4	32.6	15.8	15.2
20	-1.73	-1.71	54.7	57.3	24.9	21.8
100	-1.89	-1.89	120	118	47.2	36
200	-1.99	-1.99	157	157	58	43
500	-2.18	-2.18	240	234	82	56

**Figure 1.** Cyclic voltammograms of (1a) ($1.0 \times 10^{-3} M$) at a mercury electrode in DMF–0.1M-TEAP solutions: (a) v 20 $V s^{-1}$; (b) v 200 $V s^{-1}$

($CH_3CONHCHXCHCl_2$) seem to be in agreement with a concerted mechanism. On the other hand, if the reductions are carried out in the presence of a proton donor (5% H_2O), the formation of the hydrogenated product (2a) (which cannot have its origin in an elimination–addition process) excludes a concerted mechanism and can be explained only by the presence of a carbanionic intermediate that may later undergo protonation.

Moreover, at none of the scan rates used did the presence of the proton donor cause shifts in the potentials of the first peak of (1a and b) or considerable variations in the corresponding peak currents. In Table 2 the data for (1b) are reported as an example. The potential-determining step is not affected by the presence of water, which acts as a proton donor in a later step with respect to the electron exchange. Consequently, both in anhydrous and in water-containing DMF, the electron exchange which depolarizes the electrode causes the formation of the carbanionic intermediate. Therefore, the unsaturated product (3) has to be regarded as the result of β -elimination involving the carbanion, and not of a concerted elimination. In addition, in anhydrous DMF, the higher the scan rate, the lower the i''_p/i'_p ratio (Figures 1 and 2). This result can easily be accounted for, by admitting that, at high scan rates, the electrode potential reaches values negative enough to allow the reduction of the double bond (E''_p) in so short a time to be competitive with that

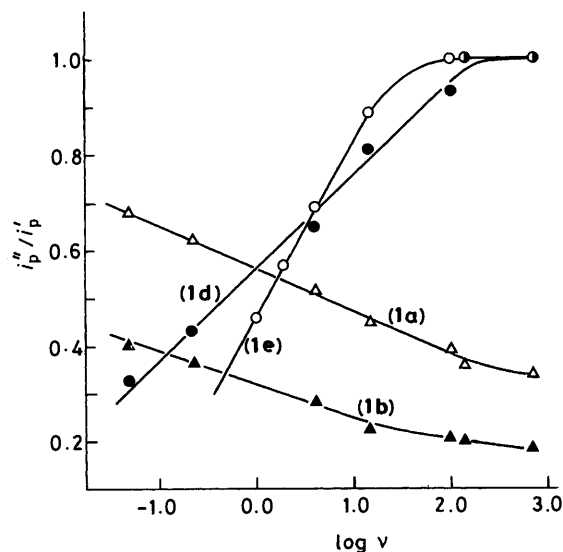
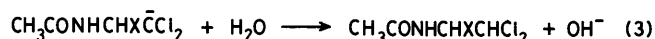
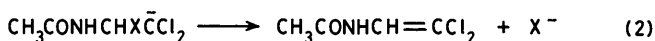
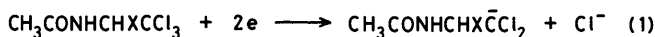


Figure 2. Variation, with the log of scan rate ($v/V \text{ s}^{-1}$), of the i_p''/i_p' ratio of the currents relative to the two reduction peaks observed in the voltammograms of compounds reported, each at $1.0 \times 10^{-3} \text{ M}$ concentration, in DMF-0.1M-TEAP solutions

taken by elimination involving the carbanions formed at E_p' and still present in the electrode-solution double layer.

The protonation of the carbanion turns out to be competitive with β -elimination only in the presence of H_2O . Under this circumstance, the possibility⁵ that the carbanion may be protonated by DMF or by the depolarizer itself has to be rejected. Furthermore, it is noteworthy that the high yield of the isolated products and the presence of 1 mol of Cl^- per mol of reduced (**1b**) exclude the carbene-forming α -elimination reaction being in any way competitive with β -elimination for these carbanions.



The formation of (**2a**) in place of the expected hydrogenated product $\text{CH}_3\text{CONHCHXCHCl}_2$ appears surprising. Compound (**2a**) does not arise from an initial transformation of (**1a**) or (**1b**) into (**1g**) followed by reduction and protonation. In fact, dimethylamine may actually promote this transformation, but not in the time span and under the conditions of our electrolyses. Moreover, the voltammograms of (**1g**) in aqueous DMF show a reduction peak at -1.65 V , which is absent in the voltammograms of (**1a** and **b**) recorded under the same conditions. Compound (**2a**) also does not arise from addition of dimethylamine to (**3**). Therefore, it seems possible that (**2a**) originates from substitution of dimethylamine on the corresponding hydrogenated products, formed at E_p' . During the electrolyses, this reaction gives higher yields in much shorter times with respect to the related chemical reaction of (**1b**). This indicates that the application of the potential strongly affects the reaction, presumably by increasing the availability of the nucleophile. We think that an explanation of these facts has to be sought in the dramatic modifications that the medium undergoes owing to reactions taking place as a consequence of the reduction at E_p' . In fact, elimination (2) as well as the

Table 3. Coulometric data and yields of the products from electroreduction (mercury cathode) of (**1a**–**f**) in DMF-0.1M-TEAP and in DMF + 5% H_2O -0.1M-TEAP^a

Compound	E/V	n_{app}	Products (% yield)
(1a)	-1.5	2.0	(3) (94)
(1a) ^a	-1.5	2.0	(3) (48) + (2a) (44)
(1b)	-1.5	1.9	(3) (80)
(1b) ^a	-1.5	2.0	(3) (44) + (2a) (36)
(1c)	-1.4	2.0	(3) (96)
(1d)	-1.8	1.9	(2b) (50)
(1d) ^a	-1.8	2.0	(2b) (88)
(1e)	-1.8	2.0	(2c) (23)
(1e) ^a	-1.8	2.1	(2c) (60)
(1f)	-1.8	2.0	(4) (15) + (5) (31)
(1f) ^a	-1.8	2.0	(4) (30) + (5) (27)

protonation reaction (3), both involving the carbanion, cause a strong build-up of carboxylate or hydroxide ion at the electrode-solution interphase. Both these ions are able to promote DMF decomposition, yielding $(\text{CH}_3)_2\text{NH}$.

It may be interesting to point out further proof that modifications in the characteristics of the diffusion layer involve variations in the electrochemical picture and in the nature and yield of the products. When voltammograms of (**1a** and **b**) are recorded in the presence of H_2O , the higher the scan rate, the higher the decrease of the current i_p'' , related to reductions of the double bond (Table 2). In fact, the modification induced in the diffusion layer owing to the reduction at E_p' (*i.e.*, a strong concentration of OH^-) also persists at E_p'' , if the electrode potential is varied at a scan rate sufficiently fast to prevent OH^- ions from back-diffusing into the bulk of the solution. On the other hand, it is known¹⁸ that the pH of the medium affects both the double bond reduction mechanism and the nature of the products.

(b) *Reduction of (1c)*. The voltammetric curves show two reduction peaks ($E_p' -1.32$, $E_p'' -2.36 \text{ V}$). Upon electrolysis carried out in anhydrous DMF at the potential of the first peak, the unsaturated product (**3**) was obtained in almost quantitative yield, and the voltammograms recorded in the solution after reduction show the presence of only one peak at -2.4 V .

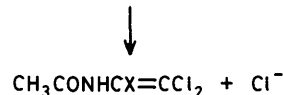
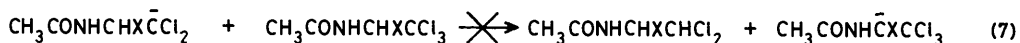
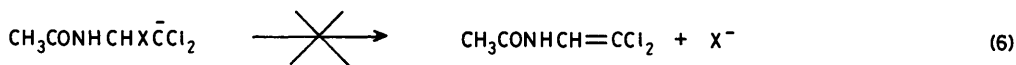
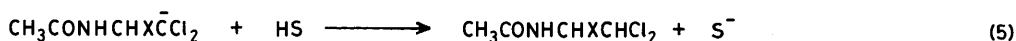
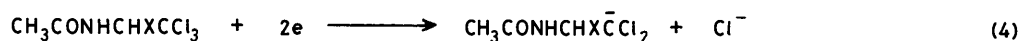
The unsatisfactory stability of (**1c**), under our conditions, prevented an accurate voltammetric investigation, similar to those carried out with (**1a** and **b**). However, the results obtained by means of the electrolysis suggest that the behaviour of (**1c**) may be qualitatively comparable with that of (**1a** and **b**).

(c) *Reduction of (1d and e)*. The voltammetric curves show two reduction peaks [(**1d**) $E_p' -1.93$, $E_p'' -2.37 \text{ V}$; (**1e**) $E_p' -1.86$, $E_p'' -2.35 \text{ V}$]. The current of the second peak fairly increases when the voltammogram is recorded in aqueous DMF solutions.

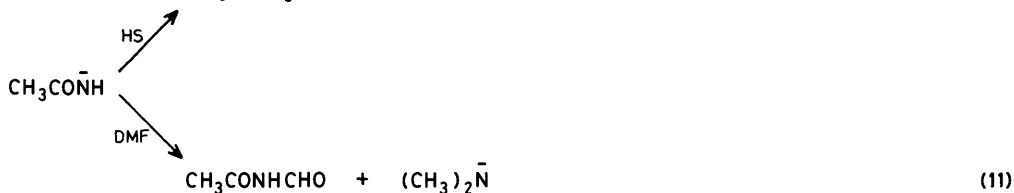
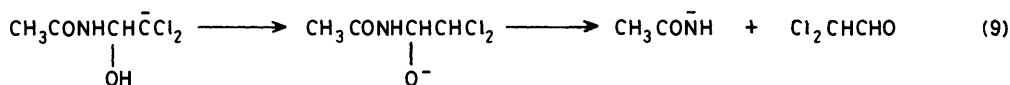
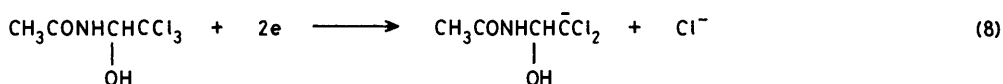
The formation of the hydrogenated products (**2b** and **c**), whose yields increase when the reduction is carried out in aqueous DMF (Table 3), points out the formation of a carbanionic intermediate and its reactivity as a base.

Moreover, the value of $n_{\text{app}} = 2$ (found also in anhydrous DMF) and the absence of unsaturated products [both (**3**) and $\text{CH}_3\text{CONHCX}=\text{CCl}_2$ -type] suggest that, for the carbanions under examination, β -elimination (6) and auto-protonation (7) are not competitive with reaction (5).

On the other hand, competition with protonation (5) seems to be provided, in this case, by α -elimination, involving the above carbanions, and yielding the corresponding carbenes. It turned out to be impossible to identify the products from such intermediates, the existence of which, however, is proven by some experimental data. In fact, the potentiometric analysis of solutions of (**1d** and **e**) after electrolysis shows the presence of 2.3



(X = OC₂H₅, Ph; HS = DMF, H₂O)



and 2.2 mol of Cl⁻ per mol of reduced substrates, respectively. Such values, clearly higher than those observed for the reduction of (1b), are in agreement with the formation of a carbene, which loses chloride ion.

Moreover, the voltammetric data for (1d and e) show that the lower the scan rate, the lower the ratio i_p''/i_p' between the currents relative to the second and first reduction peaks (Figure 2). Clearly, this datum shows a decrease in the concentration of electroactive species at E_p'' . An interpretation may be provided by considering that, at low scan rates, the electrode varies its potential from E_p' (cleavage of the first C-Cl bond) to E_p'' (cleavage of the second C-Cl bond) in a time sufficiently long to allow the spontaneous cleavage of the second C-Cl bond and the formation of a carbene. Therefore, the lower scan rate (*i.e.*, the higher the percentage of carbanions that undergo α -elimination), the higher will be the decrease in the i_p''/i_p' ratio.

(d) Reduction of (1f). The voltammetric curves show two reduction peaks ($E_p' - 1.96$, $E_p'' - 2.53$ V). The presence, in the reduced solutions, of 1.1 mol of Cl⁻ per mol of substrate and the value of $n_{\text{app}} = 2$ indicate the formation of a carbanionic intermediate. Moreover, the presence of CH₃CONH₂ (4) and CH₃CONHCHO (5) indicates that the reduction of (1f) may be described as an example of electrochemically induced N-C bond cleavage. We suggest that such cleavage has to be related to the formation of an oxygen anion from the corresponding carbanion, *via* intramolecular protonation (9).

The formation of (4) and (5) indicates the reactivity of the nitrogen anion CH₃CONH⁻ both as a base (10) and as a nucleophile (11). According to these reactions the addition of water, stronger than DMF as proton donor, increases the yield of (4) with respect to (5) (Table 3).

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