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PAPER

Electrochemical oxidation of amides of type $Ph_2CHCONHAr$†

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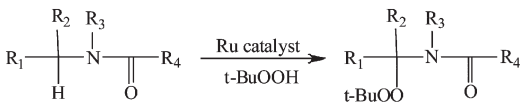
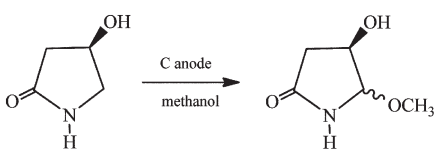
Anodic oxidation of *N*-aryl-2,2-diphenylacetamides in acetonitrile undergoes three types of bond-cleavage, one between the benzylic carbon and the carbonyl group, the second between a carbonyl and 'N', and the third between the 'N' atom and aryl group. The selectivity of the cleavage and nature of emerged products is highly dependent on the nature of substituent attached to the aryl group. For example, electron-withdrawing groups direct the benzyl–carbonyl bond-breaking whereas electron-donating substituents favor the *N*-aryl bond cleavage. The type of products obtained involve benzophenone, 2,2-diphenylacetamide, *N*-(diphenylmethylene)acetamide, *N*-(diphenylmethyl)acetamide, α-lactam (1-acetyl-3,3-diphenylaziridin-2-one, as a 1 : 1 complex with 2,4-dinitroaniline) and aniline derivatives.

Introduction

The amide bond is one of the most important bonds in nature. Yet, relatively little is known about chemical and electrochemical oxidation of organic amides. Oxidative cleavage of amides in tyrosine amide by aqueous Br_2 led to the conversion of the phenolic ring to a dienone system.[1] This reaction was found to be general and useful for selective chemical degradation of peptides. Another chemical example led to peroxidation at the α-position to the N in an amide, in the presence of a Ru catalyst:[2]



Electrochemical oxidation of monoalkylated amides and lactams in methanol has been confined mostly to methoxylation at the α-position to nitrogen. For example, (*R*)-4-hydroxy-2-pyrrolidinone undergoes methoxylation to afford an 8 : 1 mixture of *trans* : *cis* isomers, respectively:[3]



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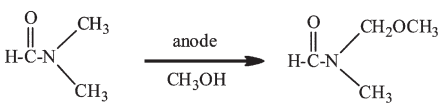
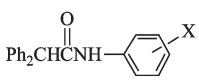
This electrochemical process is of considerable synthetic value because the products of α-methoxylation are quite stable (unlike in amines) and can be used effectively in *e.g.*, amidoalkylation reactions[4] and annulations of rings onto amines and amino acid derivatives.[5] It should be pointed out that in less common cases, where suitable electron-rich phenyl rings are present, methoxylation occurs at the α-position to the carbonyl group rather than to nitrogen.[6]

When the 'N' in the amide functionality is fully alkylated, α-alkoxylation (in alcohols) and α-acyloxylation (in acetic and formic acids) take place[7] as previously described. However, under certain conditions, tertiary amides undergo α-hydroxylation followed by oxidative dealkylation to yield secondary amides and aldehydes.[8] In addition, when no α-hydrogen is available an alternative route could take place, for example, side-chain *N*-methoxylation:[9]



The present work describes the synthesis of amides of type $Ph_2CHCONHAr$ (Scheme 1) (lacking hydrogen(s) at the α position to N), and their anodic oxidation in acetonitrile under controlled potential electrolysis (CPE). The outcome from their preparative electrolysis indicates that they undergo various types



[X = H, p-OMe, p-Me, p-F, p-Cl, p-Br, p-CN, p-NO_2, m-Me, m-CN, m-NO_2]

Scheme 1 Synthesized substituted amides for electrolysis.

of bond cleavage, depending on the nature of the substituent attached to the aniline moiety.

Results and discussion

The results of cyclic voltammetry measurements of the amides listed in Scheme 1 are summarized in Table 1. They all exhibit at least one irreversible anodic peak potential (few of them afford a second irreversible wave). The values depend on the substituents attached to aniline ring, namely electron-donating groups at the *para* position (entries 2–3) decrease the anodic peak potential (raise the HOMO energy) with respect to non-substituted amide (entry 1) whereas those of electron-withdrawing groups (entries 8–9) increase the anodic peak potential (lower the HOMO energy). The *p*-F (entry 5) affords a similar oxidation potential and comparable with the unsubstituted derivative (entry 1). This can be explained by two contradictive effects that balance each other in the current situation. Fluorine is electron-withdrawing through a σ-bond system but electron-donating through a π-system if there is electron demand from the other end of the π-system, the amide group in the present case. As expected, the *p*-Br derivative (entry 7) has a higher oxidation potential compared with the unsubstituted derivative, but strangely, that of *p*-Cl (entry 6) is comparable.

A good correlation (R^2 = 0.96) has been found (Fig. 1) between the first anodic peak potentials of the amides and σ^+ Hammett constants[10] in which the substituents participate in resonance with the aromatic ring. The linear relationship indicates that solvation plays a minor role and hardly affects the oxidation potentials. The moderate slope (~0.45) indicates that the anodic oxidation process has moderate sensitivity to substituent effects. For comparison, the correlation with σ Hammett constants was worse (R^2 = 0.90) (see ESI†), indicating that direct conjugation effects are important.

Table 1 Oxidation potentials of amide substrates[a]

Entry	Substituent	Ep_1/V	Ep_2/V
1	H	1.85	
2	*p*-OCH_3	1.47	
3	*p*-CH_3	1.71	1.82
4	*m*-CH_3	1.75	
5	*p*-F	1.83	
6	*p*-Cl	1.86	
7	*p*-Br	1.95	2.07
8	*p*-CN	2.20	
9	*p*-NO_2	2.21	
10	*m*-CN	2.02	
11	*m*-NO_2	2.10	

[a] CVs have been recorded under air atmosphere, in CH_3CN–0.1 M $LiClO_4$; substrate concentration: 1 mM; potentials are quoted *versus* Ag/AgCl reference electrode; working electrode: glassy carbon disk (ϕ = 3 mm); auxiliary electrode: a Pt wire. Scan rate: 50 mV s^{-1}.

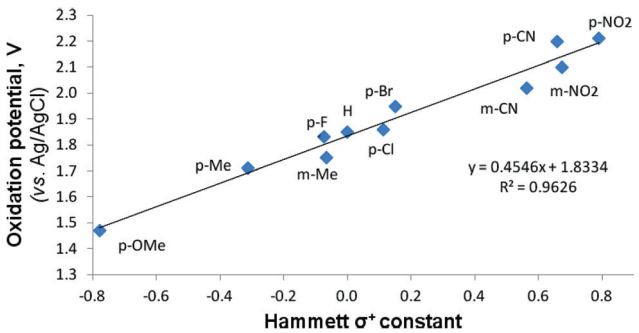
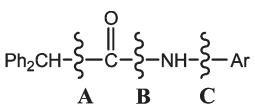


Fig. 1 Oxidation potentials *vs.* σ^+ Hammett constants.

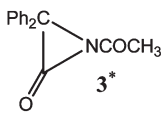
The results of preparative scale electrolysis by employing the CPE technique reveals that the studied amides (Scheme 1) undergo different types of bond cleavage (A, B and C, Scheme 2), depending on the nature of the substituent attached to the aniline moiety. The major products from 'A' type cleavage are benzophenone (**1**) and *N*-(diphenylmethyl)acetamide (**2**); from pathway 'B' an α-lactam (1-acetyl-3,3-diphenylaziridin-2-one) (**3**) and an aniline derivative (**4**), and from 'C', 2,2-diphenylacetamide (**5**). Other minor products were obtained as well, and identified as **6**, **7** and **8**.

It is noteworthy that two of the above mentioned bond cleavages ('B' and 'C') resemble the type of cleavages found in photochemistry of amides, namely Norrish types I and II processes,[11] respectively (Scheme 3).



Typical products from: **A** Ph_2CO **1**; $Ph_2CHNHCOCH_3$ **2**

B

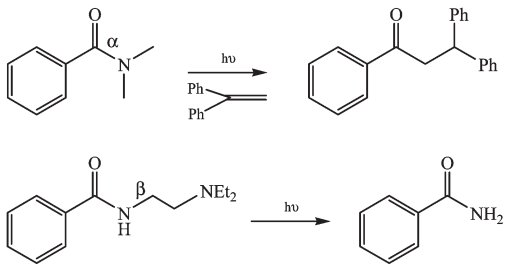


Aniline derivative **4**

C $Ph_2CHCONH_2$ **5**

Other products (minor): $Ph_2C{=}NCOCH_3$ **6**; Ph_2CHCN **7**; $Ph_2CHCOOH$ **8**

Scheme 2 Types of bond cleavage; [* **3** was trapped as complex **10** (see Scheme 8 below)].



Scheme 3 Photochemistry of amides.

Table 2 summarizes the product distribution from preparative electrolysis of all amides studied, based on the observed three types of bond cleavage. In order to afford a clearer picture of the results outlined in this table, Fig. 2 demonstrates nicely the effect of substituents on the outcome in two extreme cases of substitution compared with the non-substituted substrate. In the absence of substituent at the aryl moiety, *N*-(diphenylmethyl)-acetamide (**2**) is the major product. However, clearly, with *p*-OMe as substituent, the major product becomes 2,2-diphenyl-acetamide (**5**) whereas with a *p*-NO_2 substituent it switches to benzophenone (**1**).

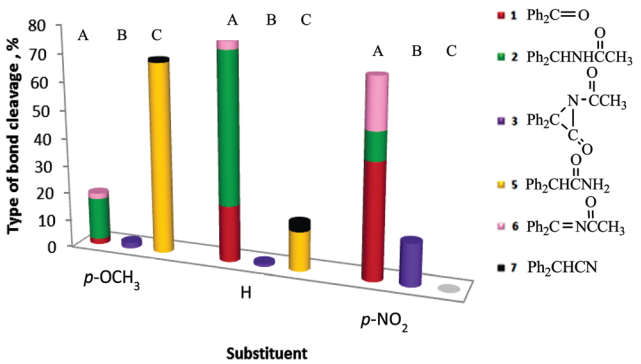
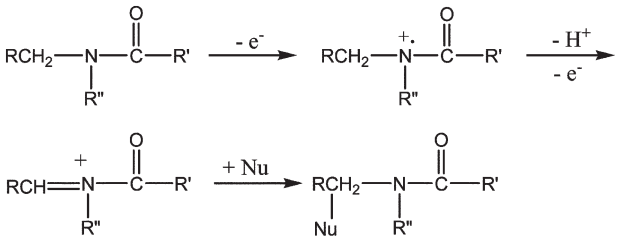


Fig. 2 Relative yields of products (by GLC).

Mechanism

It is generally accepted[12] that α-alkoxylation or esterification of amides involves an ECE mechanism by $2e^-$ oxidation, as follows:



However, in the absence of hydrogen at the α position to nitrogen the course of anodic oxidation takes different routes. The products from type 'A' bond cleavage involve mainly benzophenone, acetamido derivative and aniline. The first two products are likely to be formed *via* the intermediacy of a benzylic type carbocation, Ph_2CH^+, while aniline could be formed from the other fragment moiety of the substrate, as illustrated in Scheme 4.

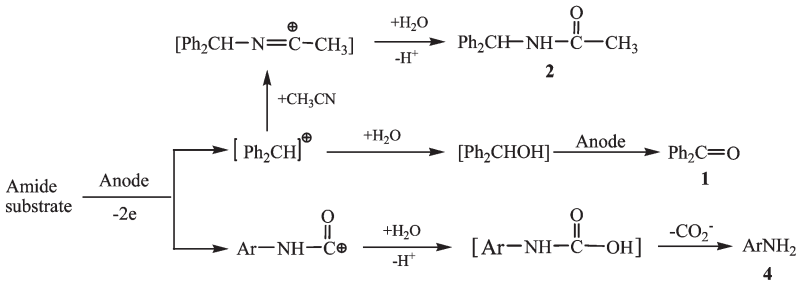
It should be pointed out that all nitro and cyano derivatives favor the formation of benzophenone (**1**) over diphenylmethyl-acetamide (**2**), both derived from the same carbocation Ph_2CH^+ intermediate. A plausible explanation is the following: both the solvent and perchlorate electrolyte are contaminated with water. It is likely that the nitro and cyano substituted derivatives form hydrogen bonding with water and as a consequence, while oxidized at the anode, bring water molecules to the vicinity of the electrode surface. Such a behavior encourages the interaction of Ph_2CH^+ cation with water rather than with the solvent acetonitrile.

Fig. 3 describes the dependence of the yield of anodic cleavage of type 'A' as a function of oxidation potential. Clearly, there is a parabolic correlation. However, two distinct groups could be identified. It appears that strong electron-withdrawing

Table 2 Product distribution from preparative controlled potential electrolysis[a]

Entry	Product[b]	H %	*p*-OMe (%)	*p*-Me[c] (%)	*m*-Me[c] (%)	*p*-F (%)	*p*-Cl (%)	*p*-Br (%)	*p*-CN (%)	*p*-NO_2 (%)	*m*-CN (%)	*m*-NO_2 (%)
1	**1**	20	2	29	15	14	25	20	38	41	47	54
2	**2**	54	15	18	44	15	36	35	29	10	20	18
3	**3**	1	2	2	0	9	16	1	7	15	3	1
4	**4**	0	0	0	0	33	0	30	1	5	4	5
5	**5**	14	68	29	15	6	8	7	5	0	6	17
6	**6**	3	2	1	4	2	3	0	11	18	7	2
7	**7**	3	1	11	10	10	10	4	3	0	5	1
8	**8**	0	0	3	4	0	0	0	0	1	1	1
9	Unreacted substrate	5	10	7	8	10	2	3	6	10	7	1

[a] Electrolysis of 1 mmol substrate was carried out in a divided cell, on a Pt foil anode, in acetonitrile–0.1 M $LiClO_4$ and was terminated when the current decayed from an initial value of ~85 mA to ~6 mA. In general, the electricity consumption was 3–4 F in order to consume most of the substrate. For example, whereas 97% of the *p*-Br derivative was oxidized after consuming 3 F, 68% and 21% was left after passing 1 F and 2 F, respectively. Also, whereas **4** was the major product after passing 1 F, **2** became the major product after consuming more than 2 F. [b] Relative yields were determined by GC. Individual products were characterized by spectral methods after column separation (see Experimental for details). [c] The *o*-Me derivative was investigated as well and found to undergo 'A' type cleavage almost exclusively, similar to the behaviour of electron-accepting substituents rather than electron-donating ones.



Scheme 4

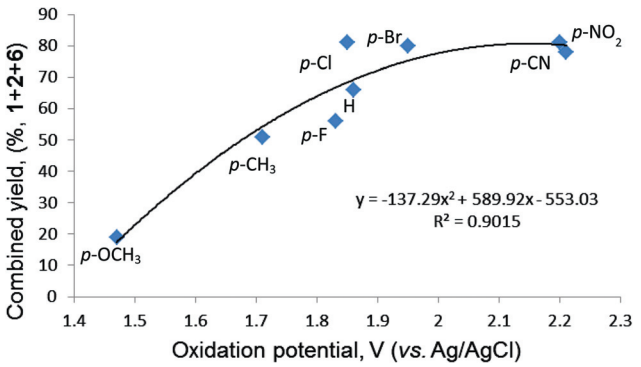
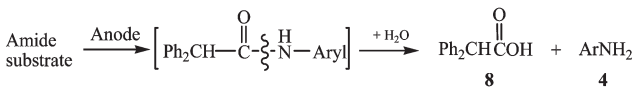


Fig. 3 Trends in anodic cleavage of type 'A'.

groups, including *p*-substituted bromine and chlorine, favor this type of cleavage more than electron-donating ones like *p*-Me and *p*-OMe; the *p*-F substituent behaves similar to the unsubstituted amide.

Type 'B' bond cleavage, the least abundant in this case, affords starting materials, as demonstrated in Scheme 5.

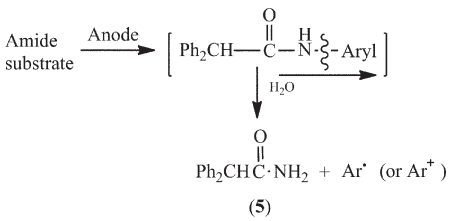


Scheme 5

It is noteworthy that this type of cleavage due to scission of the carbonyl–N bond was already observed by Mizuno and Nanya[13] when amides and lactams were anodically oxidized in acidic aqueous media to generate carboxylic acids, amino acids, ketones and imides. It seems that the anodic cleavage of this type of bond does not show a straightforward correlation between the yield of products and the oxidation potentials, as was observed *e.g.*, in Fig. 3. Although most substituents disfavor (0–3%) this cleavage, some afford 7–9% (*p*-F and *p*-CN), and some 15–16%. (*p*-Cl and *p*-NO_2). The reason for this deviation by the various substituents is not clear at present.

The products from type 'C' bond cleavage gave 2,2-diphenylacetamide (**5**) and Ar$^{\cdot}$ (or Ar^{+}), as shown in Scheme 6. The fate of the aryl moiety is not clear at present, but we do know that neither ArH nor Ar–Ar was formed.

Fig. 4 describes the yield of products by anodic cleavage of type 'C' as a function of oxidation potential. It appears that this



Scheme 6

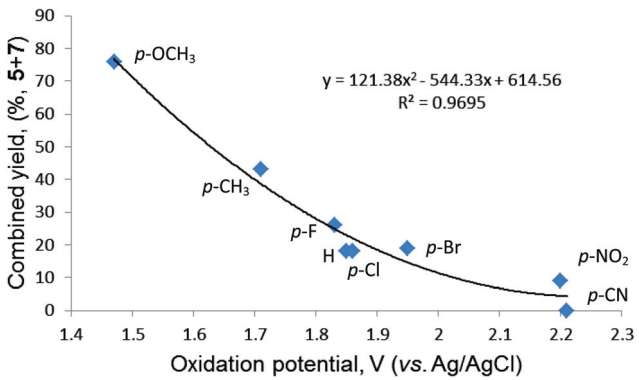
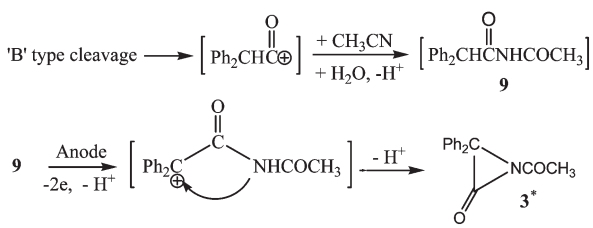


Fig. 4 Trends in anodic cleavage of type 'C'.

type of cleavage is highly promoted by a *p*-OMe group and to a lesser extent by *p*-Me one. All other substituents disfavor this type of cleavage.

Schemes 4–6 above describe the formation of products **1**, **2**, **4**, **5** and **8** but do not describe that of **3**, **6** and **7**. However, it seems that their formation is not straightforward and is not directly from the amide substrate. Therefore, it is probable that they could be formed from side reactions. Scheme 7 suggests a plausible mechanism for the formation of α-lactam **3** from **9**, an

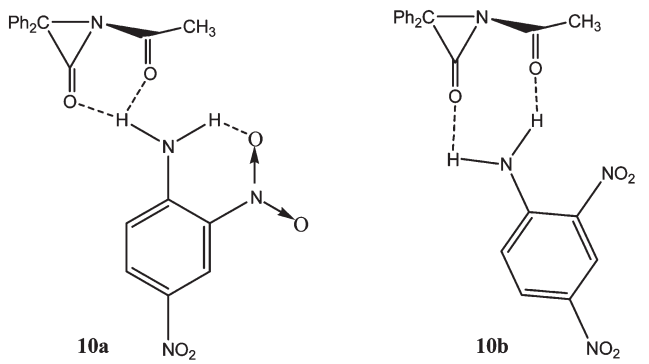


Scheme 7 (* See a footnote in Scheme 2).

intermediate product which has not been isolated separately. The scheme suggests that the anodic oxidation of **9** leads to generation of a benzylic type cation which attacks the nitrogen moiety to generate a three-membered ring by a loss of proton.

In general, α-lactams (aziridinones) have often been postulated as reactive intermediates in numerous processes because they undergo facile thermal decomposition. However in some cases, *e.g.*, this of 1,3-di-*tert*-butylaziridinone, a remarkable stability has been observed.[14] In this work, although lactam **3** was formed in low yields (0–16%, Table 2) efforts have been made to characterize it. Attempts to isolate it (*e.g.*, from the anodic oxidation of the amides substituted with *p*-Cl or *p*-CN substituents) by silica gel or neutral alumina flash chromatography (with air) resulted mostly in its decomposition on the column. Nevertheless, it could be well detected by GC-MS and high resolution ESI before column chromatography owing to its relative stability for few hours in solution (MS: *m/z* 251 (M^+), 223, 207, 194, 180 (100%), 165, 152, 139, 115, 104, 82, 43; HRMS (ESI): calculated for $C_{16}H_{14}NO_2$ + H: 252.1019; found: 252.1021). The nature of the decomposition products has been known for a long time.[15] In most cases, isocyanide and ketone (or aldehyde) are formed as major products, along with other products such as, CO, imine, nitrile, linear amide and a six-membered ring cyclic dimer, depending on the substituents.

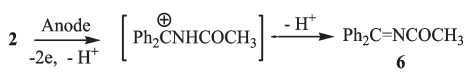
Aziridinone **3** was also formed from the *p*-NO_2 substituted amide and surprisingly, it was separated by column chromatography (silica gel) as pale yellow solid, not free, but as a 1 : 1 complex (**10**) with 2,4-dinitroaniline (for spectral evidence see Experimental). It appears that the *p*-nitroaniline used (98% purity) for the synthesis of the corresponding amide was contaminated with 2,4-dinitroaniline. Presumably, aziridinone **3** could be stabilized by hydrogen-bonding with 2,4-dinitroaniline, *e.g.*, as illustrated by forms **10a** and **10b** in Scheme 8.



Scheme 8 Postulated structures for complex **10**.

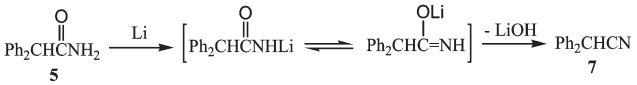
Unfortunately, so far we have been unable to obtain X-ray structure to fully characterize the complex, although it was not a major product and obtained in a low yield.

Scheme 9 describes a possible mechanism for obtaining product **6** from **2** which also involves a benzylic type cation intermediate. The driving force for this reaction could stem from achieving a higher degree of conjugation in **6**.



Scheme 9

As to the diphenylacetonitrile product **7**, in our opinion, it is likely that it could be formed by dehydration of $Ph_2CHCONH_2$ (**5**) that takes place in the cathode compartment where Li metal is generated (due to the reduction of the electrolyte $LiClO_4$), according to Scheme 10.



Scheme 10

Conclusions

Organic amides of type $Ph_2CHCONHAr$ exhibit one or two irreversible oxidation waves by cyclic voltammetry in acetonitrile. Controlled potential electrolysis at their first anodic potential reveals that they undergo different types of bond cleavage at various sites of the molecule, depending on the nature of the substituent attached to the *N*-aryl ring. The type of products obtained involves benzophenone, 2,2-diphenylacetamide, *N*-(diphenylmethylene)acetamide, *N*-(diphenylmethyl)acetamide, an α-lactam (1-acetyl-3,3-diphenylaziridin-2-one, as a 1 : 1 complex with 2,4-dinitroaniline) and aniline derivatives. In general, electron-donating groups (*e.g.*, OMe, Me) favor "*N*-aryl" bond cleavage to generate mostly $Ph_2CHCONH_2$, whereas electron-withdrawing groups (*e.g.*, CN, NO_2) promote benzylic cleavage to afford Ph_2CO and the acetamido derivative, $Ph_2CHNHCOCH_3$.

Experimental

5.1 General

NMR spectra were recorded on Bruker DPX_{200}, DPX_{400} and DPX_{500} instruments; chemical shifts, given in ppm, are relative to Me_4Si as the internal standard, or using the residual solvent peak.

MS data were obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS column, a Bruker Daltonics Ion Trap MS Esquire 3000 Plus equipped with APCI (atmospheric pressure chemical ionization) analyzed by Xcalibur software (Thermo Fisher Scientific), He gas flow 30 mL min^{-1}, column temperature from 160 to 280 °C.

Electrochemical measurements were carried out by using a Princeton Applied Research (PAR) computerized Potentiostat/Galvanostat Model 273A.

Organic compounds, reagents and solvents (analytical grade) were supplied by Aldrich, Fluka, Alfa and BioLab, and used without further purification.

5.2 Synthesis of amide substrates

The amide substrates were prepared by reacting the acid chloride of diphenylacetic acid with the corresponding aniline derivative

according to a known procedure.[16] In a typical experiment, 38.6 mmol (7.5 ml) of freshly distilled thionyl chloride was added to a 100 ml round-bottom flask containing 28 mmol (6.0 g) of diphenylacetic acid. After refluxing for 2 h the excess of thionyl chloride was evaporated. The remaining reaction mixture was dissolved in 25 ml of dry diethyl ether and 28 mmol (3.44 g) of the aniline derivative (*p*-anisidine) was added with stirring, and the reaction mixture was allowed to stand overnight. The resulting solid was filtered and washed with a 0.5 M hydrochloric acid solution. Recrystallization from ethyl acetate–petroleum ether gave an analytically pure sample. Yield of *N*-(*p*-anisyl)diphenylacetamide is 6.65 g (75%), m.p. 185–188 (lit. 188–189 °C[13]).

5.3 Cyclic voltammetry

Analytical grade acetonitrile (99.8% containing up to 0.1% water) and $LiClO_4$ (99%) were used for cyclic voltammetry (CV) measurements and controlled potential electrolysis without further purification. CV measurements were performed in a conventional three-electrode cell under air atmosphere, using 1 mM of substrate. The working electrode was a glassy carbon disk (ϕ = 3 mm), the reference electrode was Ag/AgCl (in 3 M NaCl), and the auxiliary electrode was a Pt cylindrical gauze or spiral wire. Under scan rate range of 20–400 mV s^{-1}, none of the oxidation peak potentials was reversible.

5.4 Electrolysis procedure

For controlled potential electrolysis (CPE) an H-type two-compartment cell equipped with a medium glass frit as a membrane was used. The anode compartment contained a polished silver wire quasi-reference electrode (commonly used in organic electrochemistry, approx. + 0.15 V *vs.* SCE), immersed in the electrolyte solution in a glass cylinder equipped with a fine glass frit at its end. Both compartments contained acetonitrile and 0.1 M $LiClO_4$; the analyte contained also the substrate (1 mmol in 40 mL electrolyte solution). The latter was stirred during electrolysis (4–8 h), which was terminated after passing 3–4 F, when the initial current (50–100 mA, depending on the substrate) reached a value of 5–8 mA and the unreacted starting material was 10% or less (monitored by GC-MS).

CPE was conducted by controlling the potential at the E_p value for each substrate (Table 1) (*vs.* Ag wire, which corresponds to +0.2 V *vs.* Ag/AgCl). A platinum foil (5 cm^2) working electrode and a stainless steel counter electrode were used. Pulsing (to 0 V for 1 s, every 20 s) was required during electrolysis to avoid passivation of the working electrode surface, probably due to the formation of the insulating polymer. The reaction mixture was evaporated to reach ~2 ml volume which was neutralized by saturated aqueous $NaHCO_3$ in order to transfer any residue of a carboxylic acid to the aqueous phase. The reaction mixture was extracted into 3 × 30 ml of diethyl ether. After phase separation, the organic layer was dried over $MgSO_4$ and filtered. The aqueous phase was acidified by HCl and extracted into diethyl ether, dried and filtered. The combined organic phase was subjected to GC-MS to determine the relative yields of products.

Separation and purification of products for spectral analysis was conducted by column chromatography using on silica gel (40–63 μm) and ethyl acetate–hexane as eluent. TLC analyses were performed by using Merck pre-coated silica gel (0.2 mm) aluminum [backed] sheets.

5.4 Characterization of products

Benzophenone **1**, aniline derivatives **4** and diphenylacetic acid **8** were compared with authentic samples. All other products, except for **3**, are known in the literature.

***N*-(Diphenylmethyl)acetamide (2).**[17,18] IR (KBr): A strong absorption of a carbonyl group at 1630 cm^{-1}; a broad peak of a secondary amide group at 3285 cm^{-1}; 3055, 2930, 1540, 1500, 701; ^1H NMR (in $CDCl_3$, 200 MHz) δ: 1.99 (s, 3H, CH_3), 6.22 (d, 1H, J = 8.0 Hz), 6.54 (d, 1H, J = 10 Hz), 7.15–7.37 (m, 10H), ^{13}C NMR (in $CDCl_3$, 200 MHz) δ 23.13 (CH_3), 57.04 (CH), 127.39, 128.60, 141.41, 169.51; MS: *m*/*z* 225 (M^+, 100%), 207, 182, 165, 148, 115, 106, 77, 43, 32.

2,2-Diphenylacetamide (5).[19] IR (KBr): Broad absorptions bands of primary amide group at 3180 and 3378 cm^{-1}; a strong absorption of a carbonyl group at 1650 cm^{-1}; 2944, 1500, 1400, 1253, 635; ^1H NMR (in $CDCl_3$, 200 MHz) δ 4.95 (s, 1H), 5.68 (s, 1H, NH), 6.42 (s, 1H, NH), 7.17–7.48 (m, 10H), ^{13}C NMR (in $CDCl_3$, 200 MHz) δ 58.62 (CH), 127.33, 128.77, 139.06, 141.41, 175.07; MS: *m*/*z* 211 (M^+), 193, 167 (100%), 152, 139, 115, 91, 82, 63, 44.

***N*-(Diphenylmethylene)acetamide (6).**[20,21] IR (KBr): Two absorptions of carbonyl groups at 1635 (C═N) and 1695 cm^{-1} (C═O), 2961, 2916, 2861, 1494, 1392, 1139, 1011; ^1H NMR (in $(CD_3)_2CO$, 200 MHz) δ 1.87 (s, 3H), 7.08–7.24 (m, 6H), 7.27–7.53 (m, 4H); ^{13}C NMR (in $(CD_3)_2CO$, 200 MHz) δ 23.56 (CH_3), 125.81, 126.72, 129.12, 142.85, 168.50 (C═N), 176.40 (CO); MS: *m*/*z* 223 (M^+), 208, 194, 180 (100%), 165, 152, 104, 77, 43, 32. HRMS (ESI): calculated for $C_{15}H_{13}NO$ + H: 224.1070; found: 224.1071; calculated for $C_{15}H_{13}NO$ + Na: 246.0889; found 246.0891.

2,2-Diphenylacetonitrile (7).[22,23] IR (KBr): A sharp absorption of a cyano group at 2245 cm^{-1}; 3077, 3027, 2946, 2244, 1697, 1587, 1548, 1447, 1339, 1179, 1031, 972, 778, 621, 616; ^1H NMR (in $CDCl_3$, 200 MHz) δ 5.15 (s, 1H), 7.34–7.39 (m, 10H), ^{13}C NMR (in $CDCl_3$, 200 MHz) δ 42.51 (CH), 119.68 (CN), 127.67, 128.21, 129.14, 130.01, 132.36; MS: *m*/*z* 193 (M^+, 100%), 178, 165, 152, 139, 128, 116, 89, 77, 51, 32.

A 1 : 1 complex 10 between aziridinone 3 and 2,4-dinitroaniline. IR (KBr): Two medium–weak absorptions (due to hydrogen bonding) of carbonyl groups at 1665 cm^{-1} and 1725 cm^{-1}; 3450 (broad, NH_2), 2968, 2928, 2856, 1609, 1348, 1276, 1096, 1032, 816; UV-Vis (EtOH): λ_{max} = 203, 261 and 307 nm with ε = 14 080, 4540 and 4540, respectively; ^1H NMR (in $CDCl_3$, 500 MHz) δ 2.15 (s, 3H), 7.04 (NH), 7.31–7.50 (m, 10H + NH), 8.47 (dd, 1H, J_1 = 11 Hz, J_2 = 3 Hz), 9.08 (s (br), 1H), 9.10 (d, 1H, J = 11 Hz); ^{13}C NMR (in $CDCl_3$, 400 MHz) δ 29.59 (CH_3), 71.29 (Ph_2C), 121.94, 122.11, 128.10, 128.58, 128.72, 130.01, 135.26, 139.14, 139.41, 141.83, 169.65, 170.51; MS

shows separately each components of the complex. *m*/*z* 251 (M^+ of component **3**), 223, 207, 194, 180 (100%), 165, 152, 139, 115, 104, 82, 43 and 183 (100%) (M^+ of 2,4-dinitroaniline), 167, 153, 137, 107, 91, 79, 64, 52, 32; HRMS (ESI): calculated for $C_{22}H_{18}N_4O_6$ + H: 435.1299; found: 435.1313; calculated for $C_{22}H_{18}N_4O_6$ + Na: 457.1119; found 457.1133.

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