Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 78 (6) 827–838 (2013)
JSCS–4461
UDC 547.756:66.095.252.091.7:543.552
Original scientific paper

Synthesis and electrochemical characterization of substituted indolizine carboxylates

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(Received 10 August, revised 15 October 2012)

Abstract: This work was devoted to the synthesis and characterization of new indolizine derivatives. Particular attention was paid to electrochemical investigations by cyclic voltammetry and differential pulse voltammetry. The redox processes for each compound were established, analyzed and assigned to the particular functional groups at which they occur. This assignment was based on detailed comparisons between the electrochemical behaviour of the compounds, the similarities in their structure, as well as substituent effects.

Keywords: indolizine derivatives; cycloaddition; cyclic voltammetry; differential pulse voltammetry.

INTRODUCTION

Indolizine is a π-rich system that can be easily oxidized to the radical cation.[1,2] For this reason, many indolizine derivatives showed valuable biological activity; thus they have found application in medicine and pharmacology (antimicrobial activity,[3] antioxidants,[4] cancer treatment,[5] ischemic heart disease and hypertension treatment[6]). Hence, the necessity to design new and convenient synthetic routes for compounds belonging to this class resulted in considerable efforts in the past few decades.[7–11] Indolizine derivatives are also highly luminescent,[12] this property enabling the design of fluorescent markers and sensors.[13,14] Indolizine derivatives could also find application in the design of new sensors for modern technologies,[15] due to their capacity to form surface films.[1,2] In this context, their electrochemical behaviour is, therefore, of crucial importance.

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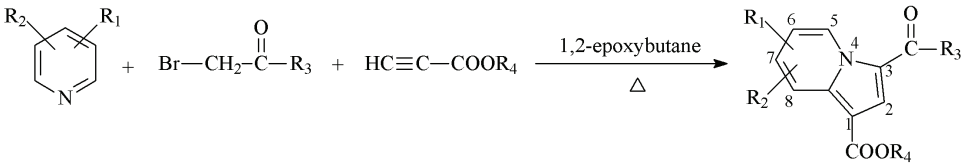
doi: 10.2298/JSC120810117S

The present work is part of a series of studies related to the electrochemical characterization of indolizine derivatives.[16] It is focused on the synthesis of new, structurally related, indolizine derivatives **IVa–e** (Table I, Scheme 1) and the study of their electrochemical behaviour. This study concerns an assessment of the electrochemical peaks related to specific redox processes that occur at the functional groups grafted on the indolizine skeleton based on their redox potentials, which are governed by their structures.

TABLE I. Structure of the studied indolizine derivatives

Compound	R_1	R_2	R_3	R_4
IVa	7-CH_3	H	C_6H_4Cl (*p*)	CH_3
IVb	7-CH_3	H	C_6H_4F (*p*)	C_2H_5
IVc	7-COC_6H_5	H	C_6H_4F (*p*)	C_2H_5
IVd	5-CH_3	8-C_2H_5	$C_6H_4NO_2$ (*m*)	C_2H_5
IVe	7-COC_6H_5	H	OC_2H_5	C_2H_5
IVf[a]	H	H	C_6H_4Cl (*p*)	C_2H_5

[a]Previously published[16]



I **II** **III** **IVa-e**

Scheme 1. General scheme for the synthesis of the indolizine derivatives.

EXPERIMENTAL

All compounds in Scheme 1, pyridine derivatives (**I**), substituted phenacyl bromides or ethyl bromoacetates (**II**), propiolic esters (**III**) and 1,2-epoxybutane were purchased from Aldrich and used without further purification. Acetonitrile and tetrabutylammonium perchlorate (TBAP), from Fluka, were used as received as the solvent and supporting electrolyte, respectively.

As a general procedure for the synthesis of indolizine derivatives, a solution of 2.5 mmol of pyridine derivative (**I**), 2.5 mmol substituted phenacyl bromide or ethyl bromoacetate (**II**), and 3 mmol of propiolic ester (**III**) in 25 mL of 1,2-epoxybutane was heated at reflux temperature for 24 h. The solvent was partly removed under vacuum, the mixture was left over night at 5–10 °C and the formed solid was filtered off and crystallized from $CHCl_3/Et_2O$.

The melting points of compounds **IVa–e** were determined on a Boetius hot plate microscope. The elemental analysis was realized on a Costech Instruments EAS 32 apparatus. The IR spectra were recorded on a Nicolet Impact 410 spectrometer in KBr pellets. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 300 BB instrument. Supplementary evidence was given by COSY (H–H) experiments. The mass spectra were obtained using a Varian 1200L Triple Quadrupole LC/MS/MS spectrometer by direct injection in ESI. Silica gel 60 and alumina (II–III Brockmann grade, 70–230 mesh ASTM) were used for the column chromatography.

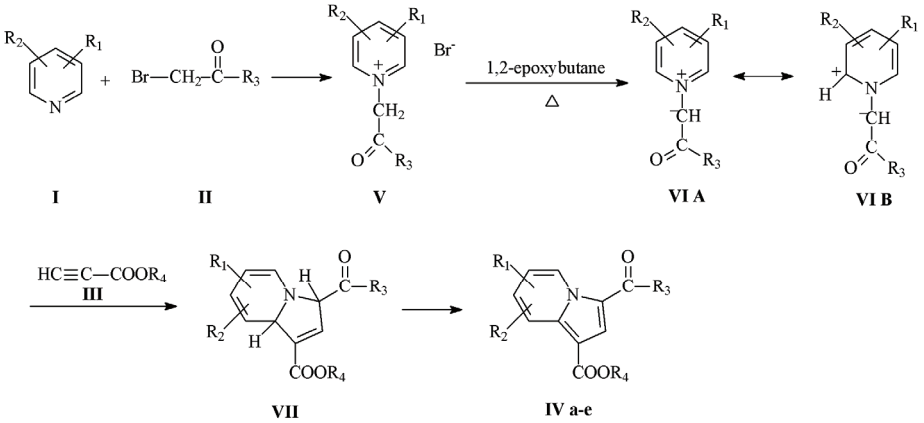
Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were employed for the electrochemical experiments using a PGSTAT12 Autolab potentiostat connected to a three-compartment cell. The CV curves were generally recorded at 0.1 V s^{-1} except when studying the influence of the scan rate in the range 0.1–1 V s^{-1}. DPV curves were recorded at 0.01 V s^{-1} with a pulse height of 0.025 V and a step time of 0.2 s. The working electrode was a glassy carbon disk (diameter 3 mm). The active surface was polished before each determination with diamond paste (200 μm). The Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN, was used as the reference electrode. The potential was referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+), which under the employed experimental conditions was +0.07 V. A platinum wire was used as the auxiliary electrode. The determinations were performed at 25 °C under an argon atmosphere.

RESULTS AND DISCUSSION

Synthesis of indolizine derivatives

Indolizine derivatives **IVa**–**e** have been prepared by one-pot, three-component procedure, developed and applied for other indolizine and azaindolizine derivatives,[17,18] starting from pyridine derivatives **I**, α-bromocarbonyl compounds **II** and electron deficient alkynes **III** in 1,2-epoxybutane, used as both reaction medium and proton scavenger (the synthetic route is shown in Scheme 1). This cycloaddition is a regiospecific process, requiring simple reaction conditions and all the final products were easily recovered by crystallization.

The reaction mechanism implies the intermediate formation of the pyridinium salts **V** from pyridine derivatives **I** and α-bromocarbonyl compounds **II** (Scheme 2). Subsequently, the bromine ion of the pyridinium salt attacks the oxirane ring of 1,2-epoxybutane, resulting in epoxide ring opening and the generation of pyridinium-*N*-ylides **VI**. The pyridinium-*N*-ylides **VI** react with the activated alkyne **III** to give the corresponding dihydroindolizines **VII** as the primary cycloadducts. Finally, by rearrangement and spontaneous *in situ* dehydrogenation of the primary cycloadduct, the indolizine derivatives **IV** are obtained.



Scheme 2. Mechanism of synthesis.

Analytic and spectral data

The structures of all the indolizine derivatives **IVa**–**e** (Table I) were confirmed by chemical and spectral analysis. The data are given in the Supplementary material to this paper.

Electrochemical studies

CV and DPV anodic and cathodic curves were recorded individually, starting from the stationary potential, for various concentrations (0–3 mM) of the studied compounds in 0.1 M TBAP/CH_3CN.

The DPV and CV curves obtained for different concentrations of **IVa** are presented in Fig. 1. Several anodic (a) and cathodic (c) processes were observed, denoted in the order in which they appeared in the voltammograms. The DPV and CV curves for increasing concentrations of **IVb**–**e** are shown in Figs. 1S–8S of the Supplementary material to this paper, respectively. The influences of the scan domain and scan rate on the CV curves are illustrated in Figs. 2 and 1S–8S. The insets in these figures show the dependences of the CV peak currents (1a, 1c and 1c′) on the square root of the scan rate. The data from all figures allow the character of each peak for **IVa**–**e** to be established (Tables II–VI, respectively).

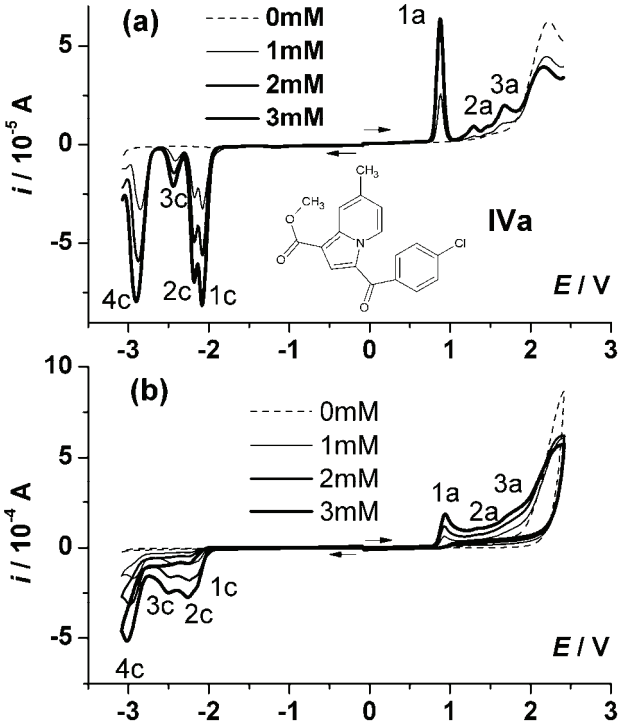


Fig. 1. a) DPV and b) CV curves for different concentrations of **IVa** in 0.1 M TBAP, CH_3CN.

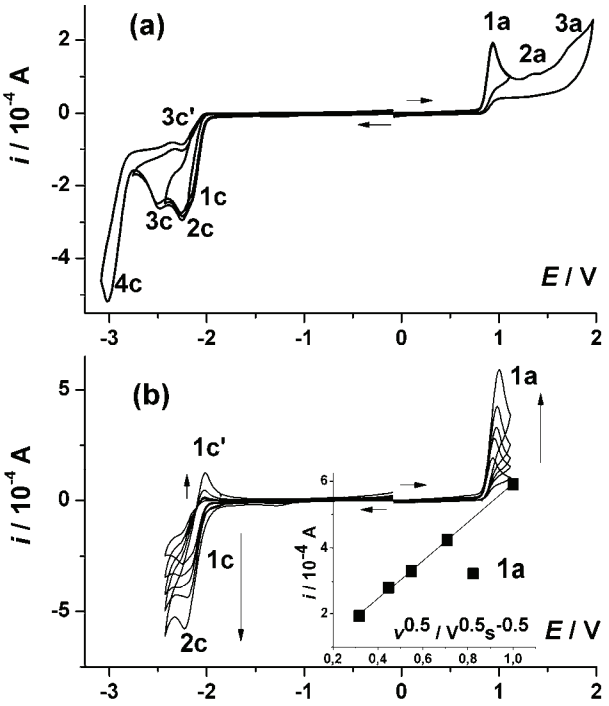


Fig. 2. CV curves for various scan domains at 0.1 V s^{-1} (a) and at different scan rates: 0.1, 0.2, 0.3, 0.5 and 1 V s^{-1} in the domains of peaks 1c and 1a (b) for **IVa** (3 mM) in 0.1 M TBAP, CH_3CN.

In order to assess the peaks obtained for **IVa**, they were compared to those of a very similar compound, ethyl 3-(4-chlorobenzoyl)indolizine-1-carboxylate, previously reported[16] and denoted **IVf**. Taking into account both the structural similarity between **IVa** and **IVf** and the specific activity potential for each functional group,[19–21] the assignments given in Table II were made for the peaks of **IVa** and **IVf** (detailed discussion further). Similarly, the redox processes for **IVb–IVe** were established using the comparison between the corresponding CV and DPV curves for: **IVa** and **IVb**, **IVb** and **IVc**, **IVb** and **IVd**, **IVe** and **IVc**, respectively. These assignments are summarized in Tables II–VI, respectively.

TABLE II. Potential (in V) and characteristics of the peaks from CV (r – reversible; i – irreversible; q – quasi-reversible) and their assignment for **IVa** and **IVf**[16]

Peak	**IVa**		**IVf**		Functional group involved / process
	DPV	CV	DPV	CV	
1a	0.873	0.941 (i)	0.951	1.008 (i)	Indolizine nitrogen / oxidation
2a	1.294	1.366 (i)	–	–	Methyl / oxidation
3a	1.673	1.746 (i)	1.733	1.800 (i)	Ketone / oxidation
1c	–2.086	–2.148 (r)	–2.065	–2.122 (r)	Ketone / reduction
2c	–2.181	–2.263 (i)	–2.164	–2.235 (i)	Halogen (Cl^-) / reduction[a]
3c	–2.444	–2.502 (q)	–2.395	–2.485 (q)	Ester / reduction
4c	–2.897	–3.015 (i)	–2.852	–2.921 (i)	Indolizine system / reduction

[a]Reductive elimination mechanism[19,20]

TABLE III. Potential (in V) and characteristics of the peaks from CV (r – reversible; i – irreversible; q – quasi-reversible) and their assignment for **IVb**

Peak	DPV	CV	Functional group involved / process
1a	0.860	0.921 (i)	Indolizine nitrogen / oxidation
2a	1.081	1.107 (i)	Methyl / oxidation
3a	1.681	1.806 (i)	Ketone / oxidation
1c	–2.183	–2.256 (r)	Ketone / reduction
2c	–2.531	–2.584 (q)	Ester / reduction
3c	–2.941	–3.035 (i)	Indolizine system / reduction

TABLE IV. Potential (in V) and characteristics of the peaks from CV (r – reversible; i – irreversible; q – quasi-reversible) and their assignment for **IVc**

Peak	DPV	CV	Functional group involved / process
1a	1.095	1.147 (i)	Indolizine nitrogen / oxidation
2a	1.768	1.935 (i)	Ketone (position 3) / oxidation
3a	2.126	2.236 (i)	Ketone (position 7) / oxidation
1c	–1.685	–1.747 (r)	Ketone (position 7) / reduction
2c	–2.043	–2.101 (q)	Ketone (position 7) / reduction-dianion
3c	–2.211	–2.287 (r)	Ketone (position 3) / reduction
4c	–2.517	–2.570 (q)	Ester / reduction
5c	–2.906	–2.995 (i)	Indolizine system / reduction

TABLE V. Potential (in V) and characteristics of the peaks from CV (r – reversible; i – irreversible; q – quasi-reversible) and their assignment for **IVd**

Peak	DPV	CV	Functional group involved / process
1a	0.816	0.862 (i)	Indolizine nitrogen / oxidation
2a	1.542	1.588 (i)	Methyl / oxidation
3a	1.721	1.765 (i)	Ketone (position 3) / oxidation
1c	–1.395	–1.447 (r)	Nitro / reduction (to NO)
2c	–1.922	–1.996 (i)	Nitro / reduction (to hydroxylamine)
3c	–2.258	–2.332 (r)	Ketone (position 3) / reduction
4c	–2.637	–2.695 (q)	Ester / reduction
5c	–2.953	–3.040 (i)	Indolizine system / reduction

TABLE VI. Potential (in V) and characteristics of the peaks from CV (r – reversible; i – irreversible; q – quasi-reversible) and their assignment for **IVe**

Peak	DPV	CV	Functional group involved / process
1a	1.084	1.133 (i)	Indolizine nitrogen / oxidation
2a	1.779	1.894 (i)	Ketone(position 3) / oxidation
3a	2.042	2.204 (i)	Esters / oxidation
1c	–1.780	–1.841 (r)	Ketone (position 7) / reduction
2c	–2.148	–2.204 (q)	Ester(position 3) / reduction
3c	–2.717	–2.797 (q)	Ester(position 1) / reduction
4c	–2.948	–3.053 (i)	Pyrrole / reduction to pyridinium salt
5c	–3.043	–3.159 (i)	Pyridinium salt / final reduction

The differences between the oxidation and reduction potentials of the two ketone groups in **IVc** could be explained by the fact that the six-membered cycle behaves as a pyridine, decreasing the electron density on the connected CO group, while the five-membered cycle, being richer in electrons, increases the electron density on the connected carbonyl group. For **IVe,** the reduction and oxidation potentials of the ester groups were established using the comparison between the DPV data for compounds **IVe** and **IVf**. The ester group in position 1 is much more conjugated than that in position 3, and was therefore harder to reduce and easier to oxidize.

It is known that indolizines are more stable when they are substituted with an electron withdrawing group at C1 (COOMe or COOEt) and they decay faster when this group is removed by reduction. However, the monoreduction to a pyridinium salt becomes possible, which generates an extra cathodic peak (5c for **IVe**) when the indolizine moiety is relatively symmetrically substituted.

The diffusion coefficients (D_0) of the new indolizines were calculated (Table VII) from the dependence of the values of currents of the first oxidation peak (**1a**) on the square root of the scan rate in CV.[22] The highest value was obtained for **IVa**, probably because this compound is less bulky as it has the lowest number of substituents.

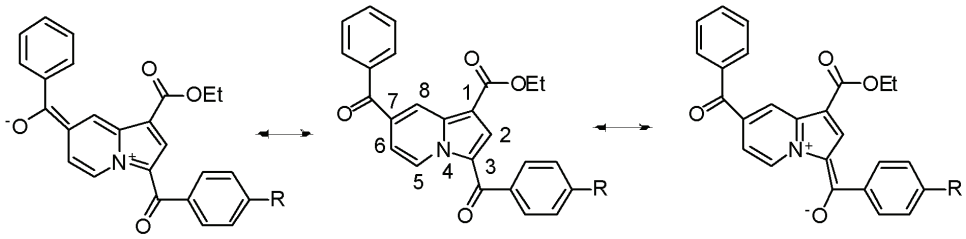
TABLE VII. Diffusion coefficients for **IVa–e**

Compound	D_0 / 10^{-5} cm^2 s^{-1}
IVa	17
IVb	5.1
IVc	6.5
IVd	2.7
IVe	5.1

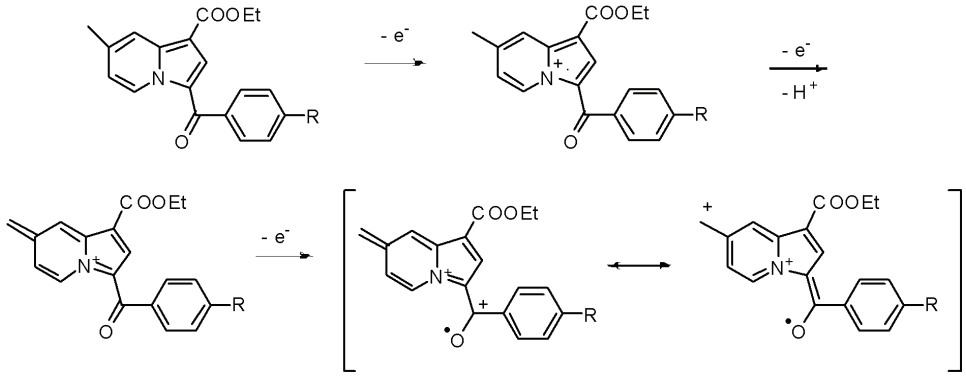
Comparison between substrates

Indolizine is an aromatic system due to its 8 π-electrons and 2 nonbonding electrons from the nitrogen atom. Therefore, the nonbonding electrons are strongly retained by the system, inducing a much higher first oxidation potential than in the cases of normal enamines. The first anodic process (1a) that is seen in the DPV and CV anodic curves is indolizine oxidation. Several remarks can be made concerning the influence of substituents (the peak potential values were taken here from the DPV experiments) on the potential of 1a. It occurs at 0.951 V in case of ethyl 3-(4-chlorobenzoyl)indolizine-1-carboxylate (**IVf**) and decreases on substitution of the indolizine ring with electron releasing groups. For instance, when Me is situated at position 7, it becomes 0.873 V in **IVa** and 0.860 V in **IVb**, while, when two alkyl substituents are present, the oxidation potential decreases even more, to 0.816 V in **IVd**. The difference between the first two potentials is determined by the intensity of the electron withdrawing power of the

aryl group linked to the keto group attached at position 3. The substituent connected to the benzoyl fragment from R_3, denoted R, can intensify the polarization of neutral molecules, decreasing their aromatic character. In fact, the ionic structures are anti-aromatic, having only 8 π electrons, as is shown in Scheme 3. Consequentially, the oxidation potentials are influenced by the nature of R and decrease when substituted in the order Cl > F. The successive oxidation steps for **IVb** are shown in Scheme 4.



Scheme 3. Limit structures for **IVc** (R = F).

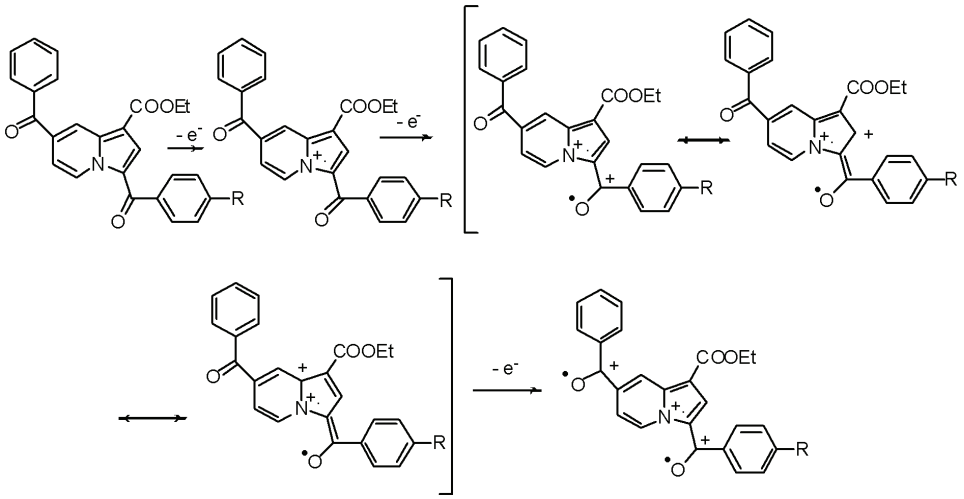


Scheme 4. Successive electron transfers in the oxidation of **IVb** (R = F).

If the PhCO electron withdrawing group is linked to the 7-position, the oxidation potential of the indolizine aromatic system increases to 1.095 V (in **IVc**) and to 1.084 V (in **IVe**). These modifications can also be easily explained by the change in the polarization of the molecule and by conjugation, which decrease the charge density on the indolizine moiety. However, in this case, the ketone group is farther in space from the nitrogen atom and, therefore, the destabilization of the aromatic character of the molecule is lower (Scheme 3).

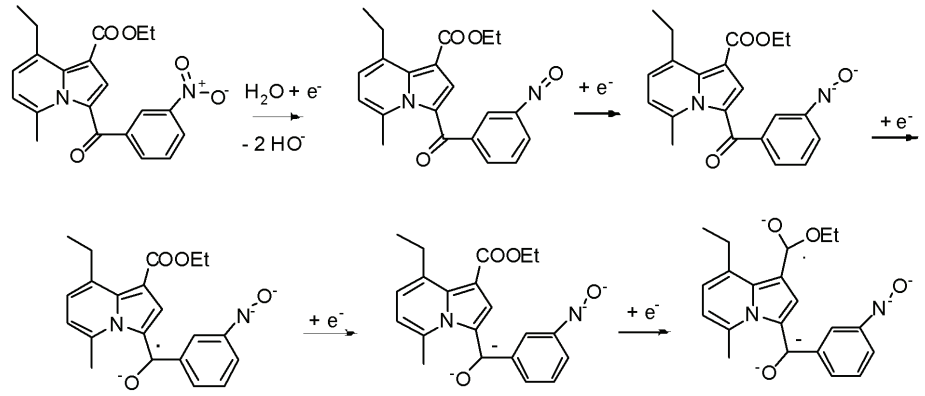
A subsequent oxidation process of these substituted indolizines is the oxidation of the ketone linked at position 3. The successive oxidation electron transfers neglecting, for the sake of clarity, the chemical steps are shown in Scheme 5. It occurs at an oxidation potential of 1.733 V in **IVf**. The presence of alkyl groups on the pyridinic moiety of indolizine decreases this potential. Their influence,

corroborated with that of the R substituent (Cl, F, NO_2), explains the variation in the oxidation potential: 1.673 V for **IVa** (R = Cl), 1.681 V for **IVb** (R = F), 1.721 for **IVd** (R = NO_2). Simultaneously, the presence of a benzoyl group at the 7-position increases this potential to 1.768 V. It is interesting that the 7-benzoyl group is oxidized at 2.126 V, a potential value much higher than that of the ketones linked to the five-member cycle. It seems that the methyl oxidation is even more influenced by the nature of the R radical. This oxidation potential increases from 1.081 to 1.294 and 1.542 V, respectively, for R = F, Cl and NO_2, these groups having different effects: +E, –I in case of F, almost only –I in case of Cl, and –E, –I in case of NO_2.



Scheme 5. Successive electron transfers in the oxidation of **IVc** (R = F).

The indolizine reduction potentials are more difficult to be rationalized because other groups are reduced faster and these redox processes affect the reduction of indolizine. Generally, the first reduction occurs at the keto group, which is reduced at –2.065 V in **IVf**. If the methyl group is linked to the 5- or 7-position, the absolute value of the reduction potential increases: –2.086 (**IVa**), –2.183 (**IVb**) and –2.258 V (**IVd**) (in this last case. the potential is also increased by the 8-Et radical). The successive reduction steps in a complex substituted indolizine, such as **IVd** (having NO_2, CO and COOEt as reducible substituents) are shown in Scheme 6. There is an initial reduction of the nitro group to hydroxylamine, followed by the reduction of the ketone group (it is possible that this step leads directly to alcohol in the presence of traces of water). The ester reductions occur at –2.395 V for **IVf**. The presence of a Me group in the 7-position increases the absolute value of this reduction potential to –2.444 (**IVa**) and –2.531 V (**IVb**).

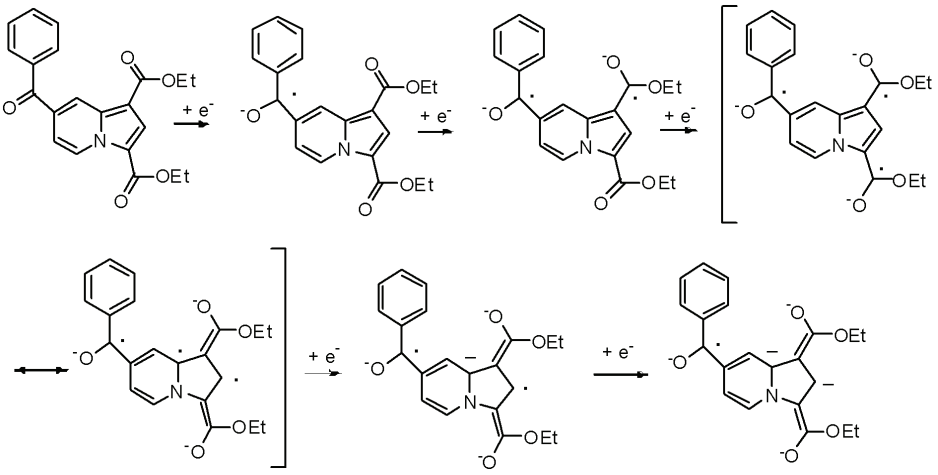


Scheme 6. Successive electron transfers in the reduction of **IVd**.

When two keto groups are present (such as in **IVc**), they are both reduced. The 7-benzoyl group is reduced easier (at –1.685 V) than that in position 3 (at –2.211 V).

The halo groups are reductively cleaved at –2.181 (**IVa**) and –2.164 V (**IVf**).

At the most negative potentials, the reduction of the indolizine system takes place, which occurs, for instance, at –2.852 V in **IVf**, while in **IVa**, **IVb** and **IVd** at –2.897, –2.941 and –2.953 V, respectively, due to the formation of negatively charged species of these compounds before reduction of the indolizine system. The same explanation is valid for **IVc** and **IVe**. The indolizine system is normally reduced at the pyrrole moiety leading to pyridinium salts (Scheme 7).



Scheme 7. Successive electron transfers in the reduction of **IVe**.

CONCLUSIONS

The investigated indolizine carboxylates presented similar electrochemical characteristics. The electron transfers of the common functional groups occurred at potentials that varied according to the substituent effect. A detailed investigation was performed to assess the processes responsible for each peak. The differences in their CV and DPV curves could be explained according to the differences in their structures. The electrochemical data helped to characterize and assess their redox processes.

SUPPLEMENTARY MATERIAL

Physical, analytic and spectral data of the compounds, as well as DPV and CV curves of glassy carbon, are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

Acknowledgements. The work has been funded by the Sectoral Operational Programme Human Resources Development 2007–2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/61178.

И З В О Д

СИНТЕЗА И ЕЛЕКТРОХЕМИЈСКА КАРАКТЕРИЗАЦИЈА СУПСТИТУИСАНИХ ИНДОЛИЗИН-КАРБОКСИЛАТА

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У раду је описана синтеза и карактеризација нових деривата индолизина. Посебна пажња је посвећена електрохемијским испитивањима цикличном волтаметријом и диференцијалном пулсном волтаметријом. За свако једињење су утврђени и анализирани редокс процеси који се одигравају у појединим функционалним групама. Оваква анализа је заснована на детаљном поређењу електрохемијског понашања једињења, сличности у њиховој структури и ефектима супституената.

(Примљено 10. августа, ревидирано 15 октобра 2012)

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