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Electrosynthesis of Cyclic α-Carbonylazo Compounds. Chemical Stability of the Electrogenerated Dienophiles and *in situ* Trapping of Dienes

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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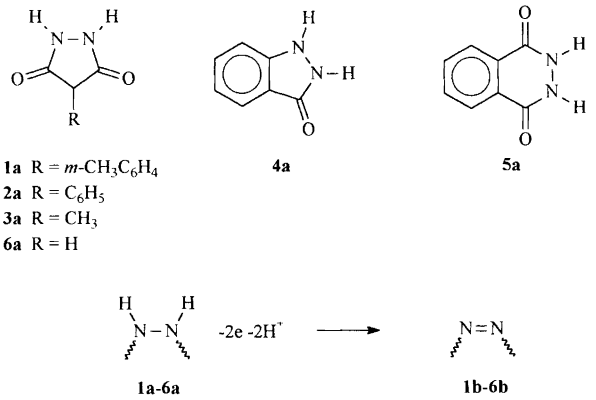
Dienophilic cyclic α-carbonylazo compounds were prepared electrochemically by oxidation of the corresponding hydrazino compounds using a flow cell fitted with a graphite felt anode in acidic methanol or acetonitrile. The instability of these compounds in methanol was first studied. *In situ* Diels–Alder additions of these electrogenerated dienophiles and various dienes were performed in relatively good yields in acidic methanol or acetonitrile.

α-Carbonylazo compounds are powerful dienophiles widely used in the construction of nitrogen containing compounds. Their use has been reviewed in the monograph of MacKenzie[1] and of Bianchi[2] and Moody.[3] The LUMO energy of N=N dienophile is lower than that reported for the corresponding alkenes[3] allowing the pericyclic reactions to proceed faster and often at ambient temperature. α-Carbonylazo derivatives are generally prepared from the corresponding hydrazino compounds using chemical oxidizing agents including lead(IV) acetate,[4,5] *tert*-butyl hypochlorite[6–8] or dinitrogen tetroxide.[9] In this paper we propose an attractive alternative electrochemical pathway leading to cyclic derivatives **1b–5b** readily obtained by the anodic oxidation of the hydrazino precursors **1a–5a**.

The reaction is performed in a flow cell at a graphite felt anode. The incipient dienophile obtained in this way can be trapped either inside the porous anode or at the outlet of the cell to give Diels–Alder adducts.

Previous studies have shown that α-carbonylazo compounds are sensitive to nucleophile in both aqueous and non-aqueous solvents. For example **2b** readily reacts with methanol to give various unidentified products.[10]

Earlier work has demonstrated that **2a**, **3a** and **6a** can be oxidized at a planar platinum electrode either in acetonitrile or in methanol.[11] Taken together, these results indicate that some improvement could be introduced concerning both the feasibility of the electrochemical method and the number of dienophiles that could be synthesized in this way.



Scheme 1.

Results and discussion

Stability of studied α-carbonylazo compounds. Electroanalytical investigations. Voltammetric investigations of urazoles **1a**, **3a** performed in aqueous sulfuric medium and at a glassy carbon electrode showed a reversible oxidation system. However, most dienes are insoluble in aqueous solution and an organic solvent such as methanol or acetonitrile is usually required to dissolve not only the diene but also the hydrazino

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compounds **1a–5a**. Therefore, a mixture of methanol and sulfuric acid (2%) was selected for the electroanalytical studies. The half-wave potentials of **1a–5a** recorded at a glassy carbon rotating disc electrode are given in Table 1.

Cyclic voltammetry of urazoles **1a–3a** performed at a scan rate of 0.02 V s^{-1} illustrated the reversible azo–hydrazo system. Macroscale electrolyses of **1a–3a** in acidic methanol were performed in a flow cell fitted with a graphite felt anode. The current intensity was calculated according to the theoretical 2 F mol^{-1} process; **1a–3a** were totally oxidized and a voltamogram recorded at the outlet solution showed neither oxidation wave (**1a–3a**) nor reduction wave (**1b–3b**). This was taken as evidence that **1b–3b** are unstable in the medium used for the electrolyses.

3-Indazolinone **4a** and 2,3-dihydrophthalazine-1,4-dione **5a** were oxidized under similar conditions to those reported for **1a–3a**. The cyclic voltamograms did not show a reversible system at 0.02 V s^{-1} which is a direct indication of the greater instability of **4b** and **5b** in acidic methanol.

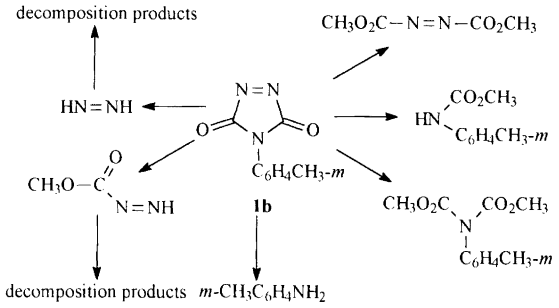
The voltamograms of **1a–3a** recorded for solutions in acidic acetonitrile did not differ significantly from those reported in acidic methanol. A reversible system was observed at a scan rate of 0.02 V s^{-1}. Macroscale electrolyses performed on a mixture of acetonitrile and sulfuric acid (2%) and in a flow cell led to a pink solution after the consumption of 2 F mol^{-1} of substrate. The presence of the triazolinediones **1b–3b** in the resulting solution was confirmed by a reduction wave recorded at a rotating disc electrode. These results provide a direct indication that triazolinediones **1b–3b** are stable under these reaction conditions and it should be noted that both the reduction wave and the pink color of the solution remained stable after storage of 24 h.

Cyclic voltammetry of 3-indazolinone **4a** in acidic acetonitrile showed a reversible system only for scan rates higher than 0.1 V s^{-1}.

Decomposition products in acidic methanol. Since **1b** and **5b** proved to be unstable in acidic methanol our first aim was to isolate and characterize the products that result from the decomposition of **1b** and **5b** under our reaction conditions. Therefore **1a** and **5a** were electrolyzed in methanol containing sulfuric acid (2%). After usual work-up and purification on a silica column several products including *m*-toluidine, *m*-tolylcarbamic acid

Table 1. Half-wave potentials ($E_{1/2}$) at a glassy carbon rotating disc electrode for the oxidation of **1a–5a** in methanol containing sulfuric acid (2%).

Compound	$E_{1/2}$ (V vs. SCE)
1a	1.3
2a	1.3
3a	1.2
4a	0.5
5a	1.0



Scheme 2.

methyl ester and *m*-tolyl-μ-dicarbonic acid dimethyl ester were isolated from the decomposition of **1b**. The formation of these species can be understood if one considers the addition of methanol to the carbonyl group followed by non-selective cleavage of the N–C=O bonds as outlined in Scheme 2. Note that the other decomposition products are postulated but were not identified.

A similar nucleophilic attack of methanol on the electrogenerated phthalazine-1,4-dione **5b** gave 1,2-dimethyl phthalate. It has previously been shown that 3-indazolone **4b** affords methyl benzoate in the presence of methanol.[12]

Diels–Alder adducts from electrogenerated α-carbonylazo compounds. In the first part of this paper voltammetric investigations showed that most of the dienophiles have limited stability in acidic methanol. However, the addition of 1,3-cyclohexadiene to a solution of indazolinone **4a** in acidic methanol caused a loss of reversibility (Fig. 1), which is a direct indication that the expected cycloaddition occurs quickly. In addition, methanol is a more convenient solvent than acetonitrile for the following reasons: price, conductivity and stability of separatory membranes.

In acidic methanol. 1,3-Cyclohexadiene and 1,3-cyclopentadiene are common cyclic dienes widely used in Diels–Alder reactions. Our first attempts were devoted to the condensation reaction between **1b** and 1,3-cyclohexadiene, mainly because 1,3-cyclopentadiene dimerizes at room temperature to give dicyclopentadiene.

Therefore, both the 1,3-cyclohexadiene and the triazolidinedione **1a** were dissolved in the reaction mixture (method A) and **1a** was oxidized at a porous graphite felt anode. A voltamogram, registered from the outlet solution, showed an oxidation wave ($E_p = 1.4$ V vs. SCE) attributed to adduct **7**. After the usual work-up procedure the crude material was purified by silica gel chromatography to afford pure **7** in 73% yield (Table 2). The fact that **7** could be oxidized at 1.4 V vs. SCE (Table 3) indicated that some improvement could be introduced in term of selectivity during the course of the electrooxidation procedure. With this aim in mind, we introduced a methanolic solution containing 1,3-cyclohexadiene at the outlet compartment of the flow cell (method B). Under

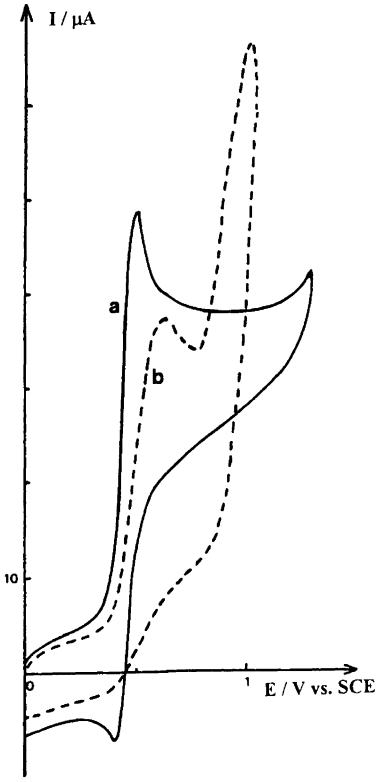


Fig. 1. Cyclic voltamogram of 3-indazolinone **4a** (4×10^{-3} M) in methanol containing sulfuric acid (2%) in the absence (a) and in the presence (b) of 1,3-cyclohexadiene (5×10^{-3} M). Vitreous carbon electrode; scan rate 0.2 V s^{-1}.

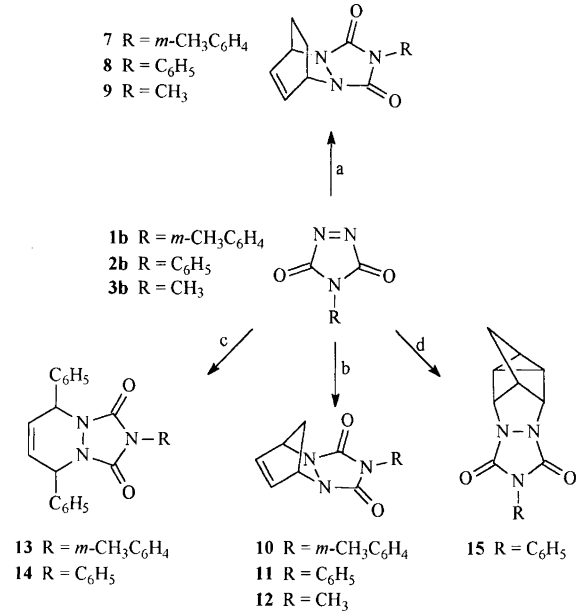
Table 2. Condensation reaction between dienophiles **1b**, **3b**, **4b**, **5b** and dienes in methanol containing sulfuric acid (2%).

Dienophile	Diene	Cycloadduct (yield, %)
1b	1,3-Cyclohexadiene	**7** (73[a], 87[b])
1b	1,3-Cyclopentadiene	**10** (70[a])
1b	1,4-Diphenyl-1,3-butadiene	**13** (50[b], 21[c])
3b	1,3-Cyclohexadiene	**9** (77[b])
3b	1,3-Cyclopentadiene	**12** (43[a], 30[b])
4b	1,3-Cyclohexadiene	**16** (65[a], 10[b])
5b	1,3-Cyclohexadiene	**17** (84[a])

[a]Dienophile electrogenerated in the presence of diene (method A). [b]Diene injected at the outlet of the porous anode (method B). [c]Diene injected at the outlet of the flow cell (method C).

Table 3. Half-wave potentials $E_{1/2}$ at a glassy carbon rotating disc electrode for the oxidation of Diels–Alder cycloadducts in methanol containing sulfuric acid (2%).

Compound	$E_{1/2}$ (V vs. SCE)
7	1.4
9	1.4
10	1.45
16	1.0
17	1.3



Scheme 3. a, 1,3-Cyclohexadiene; b, 1,3-cyclopentadiene; c, diphenylbutadiene; d, [2.2.1]hepta-2,5-diene.

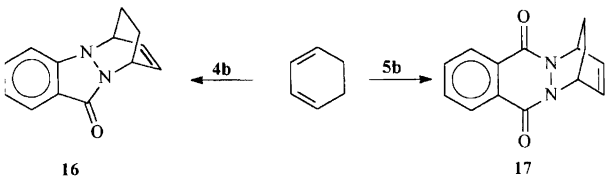
these reaction conditions the yield was raised to 87% (Table 2).

Having demonstrated that Diels–Alder adducts can be synthesized under the experimental conditions used to synthesize **7** and **9** we decided to study the behaviour of the 1,3-cyclopentadiene under our reaction conditions. In this case the reaction was carried out at room temperature with a twofold excess of diene over dienophile. The dienophile **1b** reacted with cyclopentadiene to give **10** in 70% yield.

1,4-Diphenylbutadiene was selected as a model compound to study the stereoselectivity of the Diels–Alder reaction under our experimental conditions. Prior to larger scale electrolyses, voltammetric investigations performed at a glassy carbon electrode in acidic methanol showed that 1,4-diphenylbutadiene is oxidized at a potential very close to that reported for **1a**. Moreover this diene showed little solubility in methanol. These results clearly indicate that the condensation reaction could not be performed according to method A but rather according to method B in which the diene is injected into the outlet compartment of the flow cell. Under these reaction conditions, the desired cycloadduct **13** was obtained in satisfactory yield (50%).

It should be noted that an equilibrium exists between both the *cisoid* and the *transoid* conformations of the acyclic diene. Only the *cis* form reacts with the dienophile, shifting the equilibrium as the reaction proceeds.[13] This might explain the lower reactivity observed with acyclic diene than that reported with cyclic dienes such as 1,3-cyclopentadiene or 1,3-cyclohexadiene in which the *cisoid* form is locked.

The ^{1}H NMR spectrum of the cycloadduct **13** exhibits two characteristic signals at $\delta = 5.54$ and $\delta = 6.00$ attrib-



Scheme 4.

uted to H-5, H-8 and H-6, H-7 respectively. Both the vinylic protons and benzylic protons are magnetically equivalent, which is a direct indication that **13** adopts a *cis* conformation and that the stereochemistry of the diene substituents is maintained during the Diels–Alder reaction.

Cycloadduct **16** was obtained from electrogenerated indazolone **4b** and 1,3-cyclohexadiene (Scheme 4) in a relatively good yield (65%) according to method A. Because of a low stability of **4b**, method B lead to **16** in poor yield (10%).

In spite of the instability of 1,4-phthalazinedione **5b** in acidic methanol, **5b** and 1,3-cyclohexadiene gave the cycloadduct **17** in good yield (84%) according to method A.

In acidic acetonitrile. Similar cyclocondensations to those reported in the preceding section were performed in acidic acetonitrile (Scheme 3). The stability of the dienophile in this medium makes it possible to conduct the reaction outside the cell (method C) by collecting the dienophile over a solution of various dienes. For example **2b** reacts with 1,3-cyclohexadiene to give **8** in good yield (85–90%) (Table 4). Surprisingly, the condensation reaction involving 1,3-cyclopentadiene could not be performed in acidic acetonitrile since rapid polymerisation occurs. Therefore, lithium perchlorate was selected as the supporting electrolyte. Under these reaction conditions when **2b** reacted with 1,3-cyclopentadiene, a 75% yield of **11** was obtained.

The study of homo-Diels–Alder reactions[14] is a valuable extension of our method since **2b** proved to be stable in acidic acetonitrile. The pericyclic reaction between **2b** and bicycloheptadiene proceeded sluggishly (3–4 h) affording the desired cycloadduct **15**.

Indazolone **4b** is more stable in acetonitrile than in methanol. Therefore when **4b** reacted with 1,3-cyclohexadiene, the cycloadduct **16** was obtained in good yield (80%).

Table 4. Condensation reaction between dienophiles **2b**, **4b** and dienes in acetonitrile containing sulfuric acid (2%).

Dienophile	Diene	Cycloadduct (yield, %)
2b	1,3-Cyclohexadiene	**8** (85–90[a,b,c])
2b	1,3-Cyclopentadiene[d]	**11** (75[c])
2b	1,4-Diphenyl-1,3-butadiene	**14** (57[c])
2b	Bicyclo[2.2.1]hepta-2,5-diene	**15** (46[c])
4b	1,3-Cyclohexadiene	**16** (80[c])

[a]Dienophile electrogenerated in the presence of diene (method A). [b]Diene injected at the outlet of the porous anode (method B) [c]Diene injected at the outlet of the flow cell (method C). [d]Electrolysis performed in acetonitrile–$LiClO_4$ (0.1 M).

Conclusions

Our results confirm the powerful dienophilic properties of cyclic α-carbonylazo compounds. Except for the homo-Diels–Alder reaction between **2b** and bicycloheptadiene, the compounds react quickly with the diene in acidic methanol or acetonitrile. In accordance with this property, we recently published[15] the first trapping by triazolinedione **2b** of very unstable cyclopentadienols resulting from the decomposition of ferrocenium cations in acetonitrile, in the presence of air.

The use of a flow cell with a porous anode of high specific area enabled the total and rapid oxidation of species **1a–5a** without recycling. Consequently **1b–5b** could be quickly trapped by highly reactive dienes directly inside or outside the porous anode. Therefore, in spite of the instability of the dienophilic species **1b–5b** in acidic methanol, the cycloadducts could be obtained in relatively good yields. With good control of the working potential at the anode, which is located between two counter electrodes (Fig. 2), urazoles, indazoline and 2,3-dihydrophthalazine-1,4-dione could be oxidized in the presence of dienes without oxidizing significantly the cycloadduct directly formed in the anode.

Particularly, our electrochemical method avoided oxidation by chemical reagents which can decompose the Diels–Alder adducts. Therefore we have prepared new compounds that can act as intermediates for introducing a hydrazino bridge after cleavage of the *N*-carbonyl bonds.[16]

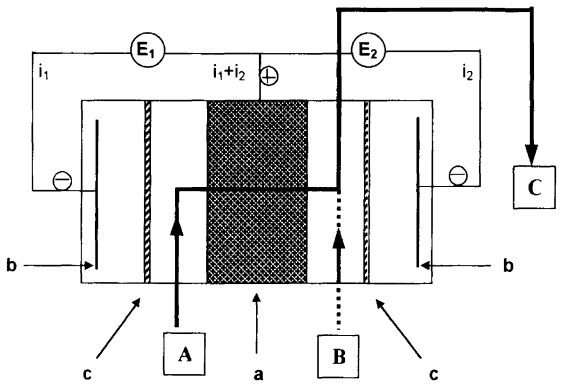


Fig. 2. Flow cell used for electrolysis of **1a–5a** and *in situ* reaction with dienes: a, porous anode; b, counter electrodes; c, diaphragms (cationic membranes); E_1, E_2, power supplies; i_1, i_2, current intensities; → electrode flow circuit (**1a–5a** injected into the inlet compartment). Method A, diene injected into the inlet compartment. Method B, diene injected into the outlet compartment. Method C, electrolyzed solution collected over diene.

Experimental

General. Melting points were determined using a Kofler apparatus and are uncorrected. The IR spectra were recorded on a Nicolet 205 FT-IR instrument for samples in CH_2Cl_2 solution. The NMR spectra were determined for solutions in deuteriochloroform with TMS as an internal reference and obtained on a Bruker AM 300 WB spectrometer at 300 MHz (^1H) and 75 MHz (^{13}C). Mass spectra were obtained on a Varian MAT 311 high resolution mass spectrometer. Elemental analyses were carried out at the *Service Central d'Analyse, Département Analyse Elémentaire CNRS* (Vernaison). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck $60F_{254}$). Column chromatography was performed on silica gel (Merck 70–230 mesh ASTM).

The starting compounds 4-substituted 1,2,4-triazolidine-3,5-diones **2a** and **3a**, 3-indazolinone **4a**, 2,3-dihydrophthalazine-1,4-dione **5a**, 1,4-diphenyl-1,3-butadiene, 1,3-cyclohexadiene and dicyclopentadiene were purchased from Aldrich. Cyclopentadiene obtained by cracking of dicyclopentadiene was used immediately. The other starting compounds were used without previous purification.

4-*m*-Tolyl-1,2,4-triazolidine-3,5-dione **1a** was prepared according to a method described in *Organic Syntheses*[17] (the presence of the CH_3 substituent made NMR analyses much easier).

4-*m*-Tolyl-1,2,4-triazolidine-3,5-dione (**1a**): m.p. 195 °C. IR (CH_3OH): $\nu = 1706\ cm^{-1}$. ^1H NMR ($CDCl_3$): δ 2.55 (s, 3 H, CH_3), 7.30–7.55 (m, 4 H arom, 2 H, NH).

Electrochemical instrumentation and procedures. Conventional electrochemical equipment was used for cyclic voltammetry and voltammetry at a rotating disc electrode (EG&G Princeton Applied Research model 362 – scanning potentiostat with an *XY* recorder). For both cyclic voltammetry and voltammetry at a rotating disc electrode, the working electrode was a disc of vitreous carbon (diameter 3 mm). All potentials refer to the saturated calomel electrode (SCE) and were not corrected for the ohmic drop. The electrolyses in a flow cell fitted with a porous graphite felt anode were performed at controlled current under a nitrogen atmosphere.[18] The electrolytic medium was a mixture of sulfuric acid (2%) and methanol or acetonitrile. The solution was pumped through the cell from a reservoir using a peristaltic pump (methanolic solution) or a membrane pump (acetonitrile solution). The flow rate (4–10 ml mn^{-1}) was measured from the outlet solution. The working electrode (5.2 cm diameter, 12 mm thickness) was made of graphite felt (Le Carbone Lorraine). The cell operated with two power supplies 0–30 V/3 A. The total current intensity i was calculated from Faraday's law according to the quantity of substrate flowing through the porous anode per second and the theoretical quantity of electricity needed; for the first electrical circuit (inlet circuit) the current intensity i_1 was 2/3 of the total current intensity ($i_1 = 2/3i$) and $i_2 = 1/3i$ for the second (outlet) circuit (Fig. 2).

General procedure for analytical electrolyses of **1a–5a** *in the flow cell.* The substrate (10^{-3} mol) was dissolved in 200 ml of the electrolysis medium (methanol or acetonitrile) containing 4 ml of concentrated sulfuric acid ($d = 1.84$). The flow electrolysis was performed with a quantity of electricity equivalent to 2 F mol^{-1} of substrate. Voltamograms from a rotating electrode (vitreous carbon) were recorded before and after electrolysis.

*Decomposition products of electrogenerated 4-*m*-tolyl-1,2,4-triazoline-3,5-dione* **1b** *in acidic methanol.* 4-*m*-Tolyl-1,2,4-triazolidine-3,5-dione **1a** (384 mg, 2 mmol) was dissolved in a mixture (200 ml) of concentrated sulfuric acid and methanol (1:49). After electrolysis in the flow cell (flow rate = 10 ml min^{-1}, $I_{ox} = 322$ mA) the resulting yellow solution was reduced in volume by half by vacuum rotary evaporation before a similar quantity of water was added. The remaining methanol was then evaporated off under vacuum. The acidic aqueous solution was extracted with CH_2Cl_2 (4 × 30 ml) before sodium carbonate was added. The resulting basic aqueous solution was extracted with CH_2Cl_2 (4 × 30 ml).

The organic solution obtained from extraction of the acidic medium was washed, dried over magnesium sulfate and concentrated by vacuum rotary evaporation. The crude reaction products were purified by column chromatography (dichloromethane) and led to *m*-tolylcarbamic acid methyl ester (80 mg, 0.48 mmol; $R_F = 0.70$; m.p. 64 °C, lit.[19] 67.5–69 °C) and *m*-tolyl-μ-imidodicarbonic acid dimethyl ester (110 mg 0.53 mmol; $R_F = 0.40$; m.p. 148 °C, lit.[19] 146–148 °C). These species were also characterized by ^1H NMR and IR spectroscopy.

The organic solution obtained from extraction of the basic medium was dried over magnesium sulfate and concentrated by vacuum rotary evaporation. The isolated *m*-toluidine was characterized by ^1H NMR and IR spectroscopy.

Decomposition product of electrogenerated phthalazine-1,4-dione **5b** *in acidic methanol.* 2,3-Dihydrophthalazine-1,4-dione (324 mg, 2 mmol) was dissolved in a mixture (200 ml) of concentrated sulfuric acid and methanol (1:49). After electrolysis in the flow cell (flow rate = 10 ml mn^{-1}; $I_{ox} = 322$ mA), the resulting pale yellow solution was reduced in volume by half by vacuum rotary evaporation before a similar quantity of water was added. The remaining methanol was then evaporated off under vacuum. The reaction mixture was extracted with CH_2Cl_2 (4 × 30 ml). The organic fraction was washed, dried over magnesium sulfate and concentrated by vacuum rotary evaporation. The crude reaction product was purified by column chromatography (dichloromethane) and led to dimethyl phthalate (298 mg, 1.54 mmol; $R_F = 0.40$) the identity of which was verified by comparison with a commercial sample.

General procedures for in situ *Diels–Alder addition of dienes to electrogenerated dienophiles* **1b–5b**. Three methods were used to introduce diene (Fig. 2).

Method A. The hydrazino compound (**1a–5a**) (3–5 mmol) and diene (4–6 mmol except for cyclopentadiene, 12 mmol) were dissolved in a mixture (200–400 ml) of concentrated sulfuric acid and organic solvent (methanol or acetonitrile) (1:49 v:v). The resulting solution was electrolyzed in the flow cell (flow rate = 10 ml min^{-1}, I_{ox} = 804 mA for 5 mmol of **1a 5a** in 200 ml).

Method B. The hydrazino compound (**1a–5a**) (3–5 mmol) was dissolved in a mixture (200–400 ml) of concentrated sulfuric acid and organic solvent (methanol or acetonitrile) (1:49) and electrolyzed in the flow cell (flow rate = 10 ml min^{-1}, I_{ox} = 804 mA for 5 mmol of **1a–5a** in 200 ml).

The diene (4–6 mmol) dissolved in methanol or acetonitrile (100 ml) (or toluene for 1,4-diphenyl-1,3-butadiene) was injected into the downstream cell compartment (flow rate = 2.5–5 ml min^{-1}).

Method C. The electrolyzed solution (200–400 ml) of dienophile (3–5 mmol) was collected at the outlet of the cell over the diene (4–6 mmol) in organic solvent (100 ml).

In all cases, the solution obtained after electrolysis was reduced in volume by half by vacuum rotary evaporation before a similar quantity of water was added. The resulting solution was neutralized with sodium carbonate, concentrated under vacuum and extracted with CH_2Cl_2. The organic fraction was dried over magnesium sulfate and concentrated by vacuum rotary evaporation. The crude reaction products were purified by column chromatography.

*2-*m*-Tolyl-4,5,8,9-tetrahydro-5,8-ethano[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3-dione* (**7**). After electrolysis of **1a** (955 mg, 5 mmol) in methanol (200 ml) according to methods A and B and reaction with 1,3-cyclohexadiene (600 µl, 6 mmol) and purification by column chromatography (dichloromethane), **7** was obtained as a white crystalline product, m.p. 176–178 °C; A: 985 mg, 73%; B: 1170 mg, 87%. IR (CH_2Cl_2) 1713 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.60 [dm, 2 H, $^2J_{AB}$ = 9.2 Hz, H_a (CH_2)], 2.21 [dm, 2 H, $^2J_{AB}$ = 9.2 Hz, H_b (CH_2)], 2.37 (s, 3 H, CH_3), 4.95 (m, 2 H, H-5, H-8), 6.51 (dd, 2 H, H-6, H-7), 7.14–7.34 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 21.4, 22.1, 50.3, 122.9, 126.4, 129.0, 129.2, 130.6, 131.3, 139.2, 156.4. HRMS $C_{15}H_{15}N_3O_2$: found 269.117 [M^+]; calcd. 269.1164.

*2-*m*-Tolyl-4,5,8,9-tetrahydro-5,8-methano[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3-dione* (**10**). After electrolysis of **1a** (955 mg, 5 mmol) in methanol (200 ml) according to method A and reaction with freshly cracked 1,3-cyclopentadiene (1 ml, 12 mmol) and purification by column chromatography (dichloromethane), **10** was obtained as a white crystalline product, m.p. 136–138 °C; 890 mg, 70%. IR (CH_2Cl_2) 1721 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.96 [dt, 1 H, $^2J_{AB}$ = 9.1 Hz, H_a (CH_2)], 2.26 [dt, 1 H, $^2J_{AB}$ = 9.1 Hz, H_b (CH_2)], 2.37 (s, 3 H, CH_3), 5.14 (td, 2 H, H-5, H-8), 6.47 (t, 2 H, H-6, H-7), 7.15–7.34 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 21.3, 48.7, 65.0, 122.8, 126.3, 129.0, 129.4, 131,1, 131.4, 139.2, 158.9. HRMS $C_{14}H_{13}N_3O_2$: found 255.100 [M^+]; calcd. 255.1008.

*2-*m*-Tolyl-4,5,8,9-tetrahydro-5,8-diphenyl[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3-dione* (**13**). After electrolysis of **1a** (955 mg, 5 mmol) in methanol (200 ml) according to methods B and C and reaction with 1,4-diphenyl-1,3-butadiene (1030 mg, 5 mmol) and purification by column chromatography (dichloromethane), **13** was obtained as a white crystalline product, m.p. 142–144 °C; B: 987 mg, 50%; C: 415 mg, 21%. IR (CH_2Cl_2) 1716 cm^{-1}. ^1H NMR ($CDCl_3$, 60 MHz): δ 2.28 (s, 3 H, CH_3), 5.50 (d, 2 H, H-5, H-8), 6.00 (d, 2 H, H-6, H-7), 7.00–7.60 (m, 14 H).

*2-Phenyl-4,5,8,9-tetrahydro-5,8-ethano[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3-dione* (**8**). After electrolysis of **2a** (531 mg, 3 mmol) in acetonitrile (400 ml) according to methods A, B and C, reaction with 1,3-cyclohexadiene (400 µl, 4 mmol) and purification by column chromatography (dichloromethane), **8** was obtained as a white crystalline product, m.p. 172 °C (lit. 172–174 °C); 650–690 mg, 85–90%. ^1H NMR ($CDCl_3$): δ 1.62 [dm, 2 H, $^2J_{AB}$ = 8.5 Hz, H_a (CH_2)], 2.23 [dm, 2 H, $^2J_{AB}$ = 8.5 Hz, H_b (CH_2)], 4.97 (td, 2 H, H-5, H-8), 6.52 (dd, 2 H, H-6, H-7), 7.26–7.45 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 22.1, 50.3, 125.6, 128.2, 129.1, 130.6, 156.2. This compound has been previously described.[20–22]

*2-Phenyl-4,5,8,9-tetrahydro-5,8-methano[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3-dione* (**11**). After electrolysis of **2a** (531 mg, 3 mmol) in acetonitrile (400 ml) containing $LiClO_4$ as the electrolyte (0.1 M) according to method C, reaction with 1,3-cyclopentadiene (1 ml, 12 mmol) and purification by column chromatography (dichloromethane), **11** was obtained as a white crystalline product, m.p. 134 °C (lit. 133–134 °C[19]); 545 mg, 75%. ^1H NMR ($CDCl_3$): δ 1.96 [dt, 1 H, $^2J_{AB}$ = 9.1 Hz, H_a (CH_2)], 2.27 [dt, 1 H, $^2J_{AB}$ = 9.1 Hz, H_b (CH_2)], 5.15 (td, 2 H, H-5, H-8), 6.47 (t, 2 H, H-6, H-7), 7.26–7.46 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ 48.9, 65.0, 125.5, 128.4, 129.2, 131.4, 131.5, 158.7. This compound has been previously described.[6,20,23]

*2-Phenyl-4,5,8,9-tetrahydro-5,8-diphenyl[1,2,4]triazolo-[1,2-*a*]pyridazine-1,3-dione* (**14**). After electrolysis of **2a** (531 mg, 3 mmol) in acetonitrile (400 ml) according to method C, reaction with 1,4-diphenyl-1,3-butadiene (618 mg, 3 mmol) and purification by column chromatography (dichloromethane), **14** was obtained as a white crystalline product, m.p. 163 °C (lit. 163 °C[24]); 650 mg, 47%. ^1H NMR ($CDCl_3$, 200 MHz): δ 5,54 (d, 2 H, H-5, H-8), 6.00 (d, 2 H, H-6, H-7), 7.00–7.60 (m, 15 H). This compound has been previously described.[24,25]

4 - Phenyl - 2,4,6 - triazapentacyclo[7.2.1.$0^{2,6}$.$0^{7,11}$.$0^{8,12}$]-dodecane-3,5-dione (**15**). After electrolysis of **2a** (531 mg, 3 mmol) in acetonitrile (400 ml) according to method C, reaction with bicyclo[2.2.1]hepta-2,5-diene (435 mg, 4 mmol) and purification by column chromatography (dichloromethane), **15** was obtained as a white crystalline product, m.p. 169 °C (lit. 171–172 °C[20]); 375 mg, 46%. This compound has been previously described.[6,20,24]

2 - Methyl - 4,5,8,9 - tetrahydro - 5,8 - ethano[1,2,4]triazolo-[1,2-a]pyridazine-1,3-dione (**9**). After electrolysis of **3a** (575 mg, 5 mmol) in methanol (200 ml) according to method B, reaction with 1,3-cyclohexadiene (600 µl, 6 mmol) and purification by column chromatography (dichloromethane), **9** was obtained as a white crystalline product; 735 mg, 77%. This compound has been previously described.[22,23]

1,4,5,11b-Tetrahydro-1,4-ethanopyridazo[1,2-a]-indazol-6-one (**16**). After electrolysis of **4a** (670 mg, 5 mmol) in methanol (200 ml) according to methods A and B, reaction with 1,3-cyclohexadiene (600 µl, 6 mmol) and purification by column chromatography (dichloromethane–methanol 9:1), **16** was obtained as a pale yellow crystalline product, m.p. 148–150 °C; A: 690 mg, 65%, B: 110 mg, 10%.

Electrolysis of **4a** (402 mg, 3 mmol) in acetonitrile (400 ml) according to method C led, after reaction with 1,3-cyclohexadiene (400 µl, 4 mmol) and purification, to **16**; 510 mg, 80%. IR (CH_2Cl_2) 1666 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.57–1.77 [m, 2 H, H_a (CH_2)], 2.21–2.32 [m, 2 H, H_b (CH_2)], 4.78 (m, 1 H, H-1 or H-4), 5.29 (m, 1 H, H-4 or H-1), 6.24–6.29 (m, 1 H, H-2 or H-3), 6.45–6.50 (m, 1 H, H-3 or H-2), 7.08 (t, 1 H, H-8), 7.18 (d, 1 H, H-10), 7.46 (t, 1 H, H-9), 7.78 (d, 1 H, H-7). ^{13}C NMR: δ 22.9, 23.7, 49.8, 53.8, 111.7, 119.7, 121.9, 124.1, 128.6, 131.8, 132.0, 150.1, 168.0. $C_{13}H_{12}N_2O$: calcd. C 73.58, H 5.66, N 13.20, O 7.54; found C 72.77, H 5.76, N 13.27, O 7.91.

1,4,5,12-Tetrahydro-1,4-ethanopyridazo[1,2-b]phthalazine-6,11-dione (**17**). After electrolysis of **5a** (810 mg, 5 mmol) in methanol (200 ml) according to method A, reaction with 1,3-cyclohexadiene (600 µl, 6 mmol) and purification by column chromatography (dichloromethane), **17** was obtained as a white crystalline product, m.p. >250 °C (lit. 300–302 °C[27]); 1010 mg, 84%. IR (CH_2Cl_2) 1628 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.73 [m, 2 H, $^2J_{AB}$ = 9.1 Hz, H_a (CH_2)], 2.17 [m, 2 H, $^2J_{AB}$ = 9.1 Hz, H_b (CH_2)], 6.03 (m, 2 H, H-1, H-4), 6.71 (m, 2 H, H-2, H-3), 7.78 (dd, 2 H, H-7, H-10), 8.32 (dd, 2 H, H-8, H-9). ^{13}C NMR ($CDCl_3$): δ 22.8, 47.4, 127.4, 132.5, 133.6, 154.1. HRMS $C_{14}H_{12}N_2O_2$: found 240.090 [M^+]; calcd. 240.0899. This compound has been previously described.[26]

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