CROATICA CHEMICA ACTA CCACAA 54 (4) 451—458 (1981)

CCA-1303

YU ISSN 0011-1643
UDC 547:587.51
Original Scientific Paper

Electrochemical Synthesis of Heterocyclic Compounds. XI.[1] Annelation of Coumarin Ring via Cathodic Reduction of 3-Nitrocoumarin Derivatives

Katmerka Tabaković and Ibro Tabaković

Faculty of Technology, »Đuro Pucar Stari« University, 78000 Banjaluka, Yugoslavia

Received April 10, 1981

Annelation of the coumarin ring was performed via cathodic reduction of 3-nitrocoumarin derivatives (**1—4**) by controlled potential. The reduction of 3-nitro-4-aminocoumarin, **1**, gave 3,4-diaminocoumarin, **5**, and subsequent treatment with formic acid furnished the novel 4H [1] benzopyrano [3,4-b] imidazole-4-on ring system **6**. The condensation of **5** with trifluoracetic acid anhydride, acetic acid anhydride, and benzil gave products **7**, **8** and **9**, respectively. The reduction of 3-nitro-4-carbetoxymethylthiocoumarin, **2**, gave the cyclic product 3H, 5H [1] benzopyrano[3,4-b]1,4-thiazine (2H)-3,5-dion, **10**. The reduction of 3-nitro-4-(2-formylphenoxy)coumarin, **3**, and subsequent intramolecular condensation of amino derivative **11** gave the novel 8H [1] benzopyrano[3,4-b]1,4-benzoxazepin-8-on ring system **13**. The same compound **13** was obtained through reduction of 3-nitro-4-chlorcoumarin, **4**, to 3-amino-4-chlorocoumarin, **12**, acid and subsequent condensation of **12** with salicylaldehyde.

Compounds having a coumarin ring possess a wide range of biological activities and show interesting chemical reactivity[2–6]. The electrochemistry of coumarin and its derivatives has also been reviewed[7]. The polarographic behaviour of 3-nitro, 3-nitroso-3-phenylazo-4-hydroxycoumarin and 3-nitro-4-aminocoumarin has been investigated recently in acid, neutral and basic solutions[8].

H. Lund described many electrochemical cyclisations leading to heterocyclic systems in which the reducible group and the unsaturated electrophilic function were present within the same molecule[9].

The present work provides new examples of the same principle, i. e. reaction of the carbonyl compound, as an electrophile, with an electrochemically generated amino group as an nucleophile.

RESULTS AND DISCUSSION

The following compounds are included in the investigation: 3-nitro-4-aminocoumarin (**1**), 3-nitro-4-carbetoxymethylthiocoumarin (**2**), 3-nitro-4-(2-formylphenoxy) coumarin (**3**), and 3-nitro-4-chlorocoumarin (**4**) (see Figure 1).

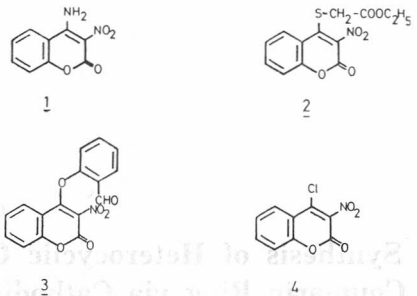

Figure 1

With all of the compounds studied well defined polarographic waves were observed. The total height of the first wave was approximately the same for all the substances compared. Comparison of the height of the first wave for compounds **1**—**4** obtained in acetic acid — 1 M aqueous HCl solution, with the wave of 3-nitro-4-hydroxycoumarin, for which the number of electrons was known[8], indicates a six-electron process, which corresponds to the reduction of the nitro to an amino group. The results of coulometry at controlled potential on the plateau of the first wave, given in Table I, varied between $n = 5.5$—6.1. The linear dependence of the limiting current on the square root of the effective height of the mercury reservoir and the concentration of the substrates showed that the currents are diffusion controlled.

TABLE I

Electroanalytical Data

Compound	$E_1/2$[a] (V vs. SCE)	i_d/C (mA M^{-1})	n-Value[b]	Potential controlled (V vs. SCE)
Compound **1**	—0.23	14	6.0	—0.50
Compound **2**	—0.10	16	6.1	—0.35
Compound **3**	—0.05	14	5.5	—0.50
	—0.95	6	2.4	—1.05
Compound **4**	—0.21	14	6.1	—0.05
	—0.98	5	1.9	—1.05

[a] 0.5—1 × 10^{-3} M concentration of the substrate in 0.5 N HCl aqueous acetic acid (50%)
[b] n — Value obtained by coulometry at controlled potential. The concentrations of the substrates varied between 1—2 × 10^{-2} M.

The second wave of 3-nitro-4-chlorocoumarin (**4**) can be attributed to the two-electron cleavage of the C—Cl bond. The reduction of **12** at controlled potential gave $n = 1.9$ F mol^{-1} and 3-aminocoumarin was isolated as a product. The second wave of 3-nitro-4-(2-formylphenoxy) coumarin (**3**) seems to involve two electron processes. The reduction of **11** at controlled potential (see Table I) gave $n = 2.4$ F mol^{-1} and 3-amino-4-hydroxycoumarin was isolated as a product.

Knowledge of the polarographic behaviour was helpful in choosing conditions for the preparative electrolysis: the large potential difference between

the first and second waves in compounds **3** and **4** made performing a selective reduction of the nitro group feasible.

Reduction of 3-nitro-4-aminocoumarin (**1**), described by V. L. Savel'ev and co-workers[10], was performed by catalytic hydrogenation using Pd/C as a catalyst. It is worth mentioning that compound **1** is actually used as a bacteriostatic agent[11]. We have applied the electrochemical procedure using constant current electrolysis with 5 to 30 grams of the starting substrate **1**. 3,4-Diaminocoumarin, **5**, was isolated in 87% yield and it seems that electrochemical reduction is a useful and simple method for the synthesis of **5**, as a suitable intermediate for further annelation of the coumarin ring (see Figure 2).

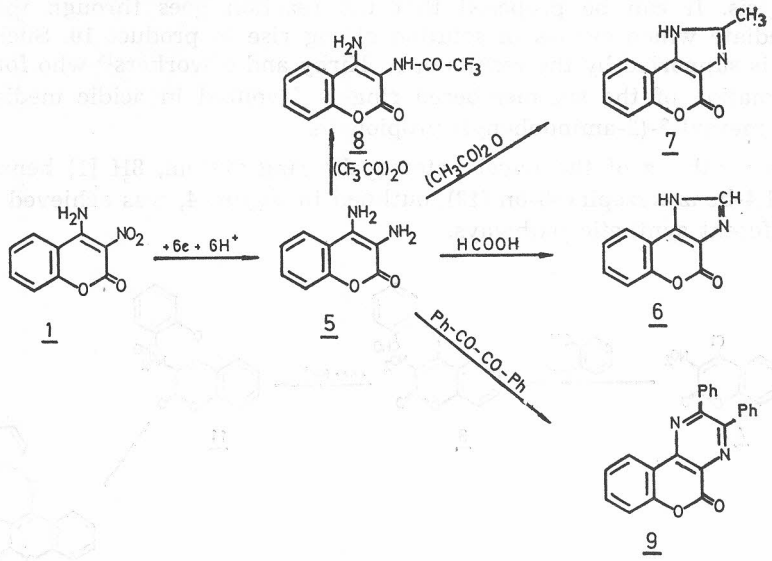

Figure 2

Compound **5** was converted to 4H [1] benzopyrano [3,4-b] imidazole-4-on, **6**, after refluxing for four hours in formic acid. Compound **6** appeared to be a novel heterocyclic ring system. Among other spectroscopic and analytical supports for structure **6**, it was shown that the molecular ion in the mass spectrum (m/e = 186) was the base peak. The further fragmentation is best explained by a primary loss of carbon monoxide from the parent compound. Compound **5** gave, after refluxing for eight hours in acetic acid anhydride, the imidazol derivative **7**, and in reaction with benzil in ethanol compound **9** was obtained. However, in the reaction of **5** with trifluoroacetic acid anhydride the cyclisation failed and 4-amino-3-trifluoroacetamidocoumarin **8** was isolated.

3-Nitro-4-chlorocoumarin, **4**, was transformed in compound **2** by using thioacetic acid ethyl ester as a nucleophile (Figure 3). It is well established[6]

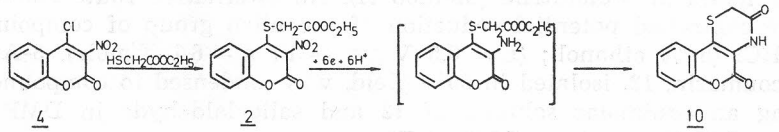

Figure 3

that Pearson's[12] HSAB concept of favorable interactions of hard acids with hard bases and of soft acids with soft bases can be applied in the case of 3-nitro-4-chlorocoumarin. According to our results[6], hard nucleophiles substituted for chlorine in position 4 and soft nucleophiles substituted for the nitro group in position 3 in the case of 3-nitro-4-chlorocoumarin, **4**. The mercapto group is considered to be a soft nucleophile and the conversion **4** → **2** is an exception to the general behaviour found with other nucleophiles. However, similar exceptions are known in the literature[13,14].

Electrolysis of **2** in 0.5 M HCl (40% ethanol) at controlled potential (E = = 0.35 V vs. SCE) consumed 6.1 F/mol., and compound **10** precipitated during electrolysis. It can be proposed that the reaction goes through the amino intermediate which cyclies in solution giving rise to product **10**. Such a conclusion is supported by the results of A. Kirby and coworkers[15] who found that the formation of the six membered ring is favoured in acidic media in the case of methyl-3-(2-aminophenyl) propionate.

The synthesis of the novel heterocyclic ring system, 8H [1] benzopyrano [3,4-b] 1,4-benzoxazepine-8-on (**13**), outlined in Figure 4, was achieved through two different synthetic pathways.

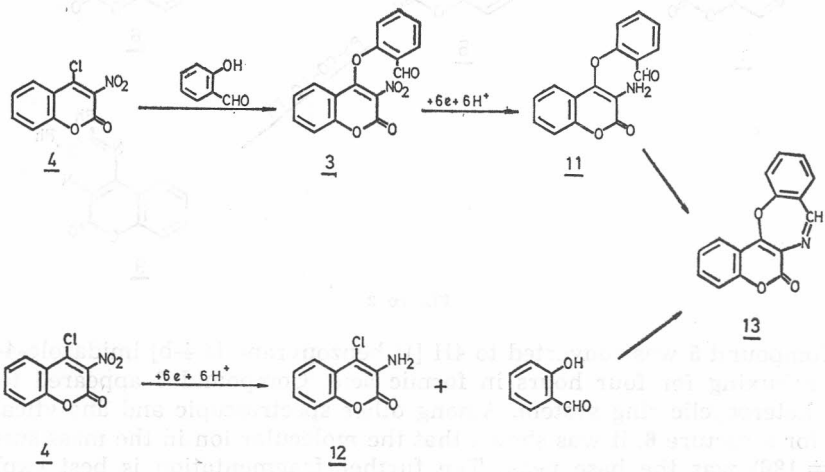

Figure 4

Treating 3-nitro-4-chlorocoumarin, **4**, with salicylaldehyde gave 3-nitro--4-(2-formylphenoxy) coumarin, **3**, which was subjected to electrolysis in 0.5 M HCl (60% ethanol) at controlled potential (E = 0.5 V vs. SCE). Electrolysis was completed after consumption of 5.5 F/mole and the amino derivative, **11**, was isolated in 61% yield. Compound **11** was converted to **13** after refluxing for four hours in acetonitrile (Method A). An alternative route started with selective controlled potential reduction of the nitro group of compound **4** in 0.5 M HCl (60% ethanol); (E = 0.5 V vs. SCE; n = 6.1 F/mole). 3-Amino-4--chlorocoumarin, **12**, isolated in 59% yield, was condensed to compound **13** by refluxing an equimolar solution of **12** and salicylaldehyde in DMF in the presence of NaH as a base (Method B).

Knowledge of the polarographic behaviour made it possible to predict suitable reaction conditions and avoid overreduction by control of the potential. It was shown that the electrochemical method is a convenient route for annelation of the coumarine ring via cathodic reduction of 3-nitrocoumarin derivatives.

EXPERIMENTAL

Polarograms were recorded on a Polariter PO-4 polarograph (Radiometer Copenhagen). The cell used was of a modified H-type of 25 ml capacity with a dropping mercury electrode and saturated calomel electrode connected via a salt bridge of 3% agar in saturated chloride solution. Electrolysès at controlled potential were carried out by means of a potentiostat (Amel-555-54). The current was measured by an electronic integrator until it dropped to 1—3% of its starting value, and the number of electrons transferred during each experiment was calculated. Preparative electrolysès were performed in the H-type cell previously described unless stated otherwise[16]. The cathode was a mercury pool (40 cm^2) and graphite was used as the anode. A saturated calomel reference electrode was connected to the cathode compartment through a Luggin capillary. All electrolysis were carried out under a nitrogen atmosphere.

Melting points were determined on a Kofler-microheating stage and are uncorrected. NMR-spectra were obtained on a Perkin Elmer R 12A spectrometer, using TMS as an internal standard. IR spectra were recorded on a Perkin Elmer M-377 spectrometer (KBr-pellets) and the mass spectra were obtained from a Hitachi Perkin-Elmer RMV-G1.

Starting materials — 3-Nitro-4-chlorocoumarin, (**4**),[10] and 3-nitro-4-aminocoumarin, (**1**),[10] were prepared according to the literature directions.

3-Nitro-4-carbetoxymethylthiocoumarin, (2)

3-Nitro-4-chlorocoumarin (0.1 g, 4.4 mmol) was dissolved in 50 ml of acetonitrile. Thioacetic acid ethyl ester (0.52 g, 4.4 mmol) and 1.65 g (1.5 mmol) of triethylamine were added to the solution and the mixture was refluxed for 2 hours. The solvent was evaporated and the resulting yellow oil after recrystalization from ethanol--water (3 : 7) gave 0.89 g (66%) of **2**, m. 53—54 °C.

IR (KBr-pellet): 3060 ($CH_{arom.}$), 2970, 2910 ($CH_{aliph.}$), 1725 (pyrone C=O), 1600 (C=$C_{arom.}$), 1540 ($NO_{2arom.}$), 770 cm^{-1}; NMR (DMSO-d_6): δ = 7.5—8.5 (m, $4H_{arom.}$), 4.15 (q, 2H, CH_2), 4.1 (s, 2H, CH_2), 1.2 (t, 3H, CH_3) ppm.

Anal. for $C_{13}H_{11}NO_6S$ (309.2) calc'd: C 50.49; H 3.58; N 4.52%
found: C 50.30; H 3.21; N 4.84%

3-Nitro-4-(2-formylphenoxy) coumarin (3)

3-Nitro-4-chlorocoumarin (1.0 g, 4.4 mmol) was dissolved in 50 ml of benzene. Salicylaldehide (0.53 ml, 4.4 mmol) and triethylamine (0.60 g, 4.4 mol) were added to the solution and the mixture was relfuxed for 7 hours. During this period, the crude, triethylamine hydrochlorice salt crystallised and was separated by suction of the mixture. Crude **3** crystallized slowly from the solution on standing at room temperature. Recrystallization from benzene gave 0.84 g (62%) of **3**, m. p. 180—182 °C.

IR (KBr-pellet): 2890 (aldehyde CH), 1750 (aldehyde C=O), 1695 (pyrone C=O), 1605 (C=$C_{arom.}$), 1530 ($NO_{2arom.}$), 770 cm^{-1}: NMR (DMSO-d_6): δ = 10.6 (s, 1H, aldehyde CH), 8.3—7.2 (m, 3H, arom.) ppm.

Anal. for $C_{16}H_9NO_6$ (311.17) calc'd: C 61.75; H 2.89; N 4.50%
found: C 61.88; H 2.70; N 4.15%

3,4-Diaminocoumarin (5)

The electrochemical reduction of **1** was performed in a laboratory beaker (2000 ml), used as a cell, provided with a diaphragm, a mercury-pool cathode (150 cm^2), and a graphite anode, as previously described[16]. The catholyte was made up of 450 ml glacial acetic acid and 450 ml 1 M aqueous HCl; the anolyte was 50 ml of 0.5 M aqeous HCl. Compound **1** (5 g) was suspended in the catholyte and reduction was

carried out with constant current density (0.01 A/cm²). After 4.5 hours, which was the theoretically required time, the electrolysis was completed. The content of the cathode compartment was removed and concentrated to a volume of about 20 ml under reduced pressure. The remaining solution was neutralized with aqueous sodium hydroxide and left standing for one hour.

The resulting precipitate of **5** was filtered off: 0.37 g (87%). Recystallization from ethanol gave pure **5** with m. p. 203—205. (Lit.[10] m. p. 203—205 °C).

IR (KBr-pellet): 3360 and 3240 (NH_2), 3060 ($CH_{arom.}$), 1675 (pyrone C=O), 1615 (C=$C_{arom.}$), 750 cm^{-1}. NMR (DMSO-d_6): δ = 7.0—8.0 (m, 4H, arom.), 6.29 (s, 2H, NH_2), 4.16 (s, 2H, NH_2) ppm.

Anal. for $C_9H_8N_2O_2$ (176.1) calc'd: C 61.36; H 4.57; N 15.89%
found: C 61.08; H 4.28; N 16.20%

4H [1] Benzopyrano [3,4-b] imidazole-4-on (**6**)

3,4-Diaminocoumarin (0.5 g, 2.8 mmol) was dissolved in 25 ml of formic acid and the mixture was refluxed for 4 hours. The solvent was evaporated and resulting crude mixture was filtered off and washed with 10 ml of 10% ethanolic HCl. Recrystallization from the mixture CH_3COOH—H_2O (1 : 1) gave 0.42 g. (80%) of **6**, m. p. 298—300 °C.

IR (KBr-pellet): 3395 (NH), 3015 ($CH_{arom.}$), 1780 (pyrone C=O), 1645, 1605 (C=$C_{arom.}$), 755 cm^{-1}. NMR (DMSO-d_6): δ = 8.38 (s, 1H, CH). 7.3—8.1 (m, 5H, NH, arom.) ppm. MS: m/e (relative intensity): 186 (100), 158 (18.4), 131 (24.1), 115 (10.3), 103 (48.3), 94 (8.0), 76 (47.1), 75 (14.9).

Anal. for $C_{10}H_6N_2O_2$ (186.1) calc'd: C 64.52; H 3.24; N 15.04%
found: C 64.50; H 3.51; N 14.96%

4H [1] Benzopyrano [3,4-b] 2-methylimidazole-4-on (**7**)

3,4-Diaminocoumarin (0.5 g, 2.8 mmol) was dissolved in 10 ml of acetic acid anhydride and the solution was refluxed for 8 hours. The reaction mixture was allowed to cool slowly, and upon reaching ambient temperature was poured into ice-cold water (150 ml). The resulting precipitate of **7** was filtered off: 0.4 g (78%). Recrystalization from ethanol gave pure **7** with m. p. 335°.

IR (KBr-pallet): 3395 (NH), 3050 ($CH_{arom.}$), 2940 (CH_3), 1730 (pyrone C=O), 1610 (C=$C_{arom.}$), 750 cm^{-1}. NMR (DMSO-d_6): δ = 8.72 (broad s, 1H, NH), 8.08—8.72 (m, 4H, arom.), 1.93 (s, 3H, CH_3) ppm. MS: m/e (relative intensity): 200 (100), 199 (8), 186 (2), 176 (4), 173 (10), 155 (4), 145 (16), 112 (8), 103 (20), 102 (8), 87 (10), 76 (24).

Anal. for $C_{11}H_8N_2O_2$ (200.1) calc'd: C 66.00; H 4.02; N 13.98%
found: C 66.26; H 3.96; N 13.54%

3-Trifluoroacetamido-4-aminocoumarin (**8**)

3,4-Diaminocoumarin (0.5 g, 2.8 mmol) was heated in 6 ml of trifluoroacetic acid anhydride for 6 hours. The reaction mixture was allowed to cool and upon reaching ambient temperature was poured into ice-cold water. The resulting precipitate of **8** was filtered off: 0.3 g (56%). Recrystallization from ethanol gave **8** with m. p. 289—290 °C.

IR (KBr-pellet): 3310, 3295 (NH, NH_2), 1710 (pyrone C=O), 1660 (amide C=O), 1605 (C=$C_{arom.}$), 755 cm^{-1}. NMR (DMSO-d_6). δ = 10.1 (broad s, 1H, NH), 8.1 (d, 2H, NH_2), 7.1—7.8 (m, 4H, arom.), ppm. MS. m/e (relative intensity): 272 (100), 225 (26), 204 (10.5), 203 (68), 176 (6), 175 (32), 148 (18.5), 147 (34), 120 (21), 102 (13), 95 (5), 91 (8), 77 (10), 76 (78).

Anal. for $C_{11}H_7N_2O_3F_3$ (272.1) calc'd: C 48.54; H 2.58; N 10.28%
found: C 48.32; H 2.70; N 10.52%

5H [1] Benzopyrano [3,4-b] 2,3-diphenylpyrazine-5-on (**9**)

3,4-Diaminocoumarin (0.5 g, 2.8 mmol) was dissolved in 50 ml of ethanol. Benzil (0.59 g, 2.8 mmol) and a few drops of 2N aqueons KOH were added to the solution

and the mixture was refluxed for 0.5 hour. The reaction mixture was left standing for 1 hour and product **9** precipitated and was separated by suction: 0.43 g (86%). On recrystallization from ethanol, pure **9** was obtained, m. p. 204—205 °C.

IR (KBr-pellet): 3060, ($CH_{arom.}$), 1745 (pyrone C=O), 1610 (C=$C_{arom.}$), 750 cm^{-1}. NMR (DMSO-d_6): δ = 7.15—8.65 (m, 14H, arom.) ppm.

Anal. for $C_{23}H_{14}N_4O_2$ (350.3) calc'd: C 78.85; H 4.02; N 7.99%
found: C 78.80; H 4.32; N 7.76%

3H, 5H [1] Benzopyrano [3,4-b] 1,4-thiazine (2H)-3,5-dion (**10**)

Compound **2** (0.7 g, 2.2 mmol) was reduced at —0.35 V vs SCE in 250 ml of 0.5 N HCl containing 40% ethanol. The reduction consumed about 6 F/mole (Table I.). During electrolysis, product **10** precipitated and was separated by suction: 0.45 g (88%). On recrystallization from ethanol pure **10** was obtained, m. p. 275—277 °C.

IR (KBr-pellet): 3340 (NH), 2920 (CH_2), 1700 (pyrone C=O), 1670 (amide C=O), 1605 (C=$C_{arom.}$), 760 cm^{-1}. NMR (DMSO-d_6): δ = 10.25 (broad s, 1H, NH) 7.3—7.7 (m, 4H, arom.), 3.25 (s, 2H, CH_2) ppm.

Anal. for $C_{11}H_7NO_3S$ (233.1) calc'd: C 56.66; H 3.01; N 6.00%
found: C 56.89; H 3.18; N 6.21%

3-Amino-4-(2-formylphenoxy) coumarin (**11**)

Compound **3** (0.7 g, 2.2 mmol) was reduced at —0.4 V vs. SCE in 250 ml of 0.5 N HCl containing 60% acetic acid. The reduction consumed about 6 F/mole. Most of the solvent was evaporated in vacuo, the pH adjusted to 7—8 with NaOH, and the precipitate filtered off: 0.38 g (61%). On recrystallization from ethanol pure **11** was obtained, m. p. 184—186 °C.

IR (KBr-pellet): 3400, 3390 (NH_2), 2930 ($CH_{aldehyde}$), 1805 (aldehyde C=O), 1710 (pyrone C=O), 1605 (C=$C_{arom.}$), 760 cm^{-1}.

3-Amino-4-chlorocoumarin (**12**)

Compound **4** (1 g, 4.4 mmol) was reduced at —0.5 V vs. SCE in 250 ml of 0.5 N HCl containing 60% ethanol. The reduction consumed about 6 F/mole. During electrolysis the orange crystals of an unidentified compound, having m. p. 270—272°, were precipitated (~0.2 g) and were separated by suction. Most of the filtrate solvent was evaporated in vacuo, the pH adjusted to 7—8 with NaOH, and the precipitate filtered off: 0.5 g (59%). On recrystallization from acetic acid pure **12** was obtained, m. p. 139—141 °C.

IR (KBr-pellet): 3450, 3350 (NH_2), 1705 (pyrone C=O), 1630 (C=$C_{arom.}$), 755 cm^{-1}. NMR (DMSO-d_6): δ = 6.9—8.0 (m, 4H, arom.), 5.25 (broad s, 2H, NH_2) ppm.

Anal. for $C_9H_6O_2Cl$ (195.6) calc'd: C 55.26; H 3.08; N 7.15%
found: C 55.41; H 3.07; N 7.22%

8H [1] Benzopyrano [3,4-b] 1,4-benzoxazepin-8-on (**13**)

Method A. Compound **11** (0.3 g, 1.06 mmol) was dissolved in 60 ml of acetonitrile, a few drops of pyperidine were added, and the solution was refluxed for 4 hours. The reaction mixture was allowed to cool and then poured into ice-cold water (150 ml). The resulting precipitate of compound **13** was filtered off: 0.16 g (61%).

Method B. Compound **12** (0.3 g, 1.53 mmol) was dissolved in 20 ml of dry DMF, and salicylaldehyde (0.18 g. 1.53 mmol) was added. The solution was refluxed for 1.5 hours and the reaction mixture was allowed to cool; upon reaching 70 °C, a small amount of NaH (0.05 g) was added, and the reaction was prolonged for another 2 hours. The solution was allowed to cool at room temperature and was poured into ice-cold water (200 ml) and neutralized with aqueous HCl solution. The precipitate was filtered off: 0.25 g. (64%) and recrystallization from cyclohexane gave pure **13** with m. p. 130—131°.

IR (KBr-pellet): 2910, (CH) 1710 (pyrone C=O), 1610 (C=$C_{arom.}$) 760 cm^{1-}. NMR (DMSO-d_6) δ = 8.1 (s, 1H, CH), 7.1—7.8 (m, 8H, arom) ppm. MS: m/e (relative inten-

sity) 263 (63.5), 262 (100), 238 (21) 210 (81.7), 211 (18.5), 192 (19.2), 181 (45.2), 165 (10.6), 153 (12.5), 152 (22.1), 122 (10.6), 121 (74), 120 (12.5), 107 (14), 105 (11), 104 (12.5), 91 (18.3), 77 (31.7), 76 (41.3).

Anal. for $C_{16}H_9NO_3$ (263.2) calc'd: C 73.28; H 3.07; N 5.33%
found: C 73.30; H 3.02; N 5.56%

REFERENCES

1. Part X in serie: M. Batušić, I. Tabaković, and S. Crljenak, *Croat. Chem. Acta* (1981) in press.
2. G. Fewrer in *Progress in Medicinal Chemistry* Vol. **10**. Elsevier, Amsterdam, p. 85 (1974).
3. N. Campbell in *Chemistry of Carbon Compounds*, E. H. Rodd Vol. *IV* **B**, Elsevier, Amsterdam, ch VIII (1959).
4. F. M. Dean *Naturally Occuring Oxygen Ring Compounds*, Butterworts, London (1963).
5. A. Mustafa, *Furopyrans and Furopyrons*, Wiley Interscience, New York N. Y. (1967).
6. K. Tabaković, Ph. D. Thesis, »Djuro Pucar Stari« University, Banjaluka (1980).
7. Ju. E. Orlov, *Usp. Khim.* **46** (1977) 1302.
8. Z. Stunić, M. Trkovnik, and M. Laćan, *Electrochim. Acta* **24** (1979) 851.
9. H. Lund, *Advan. Heterocycl. Chem.*, **12** (1970) 237.
10. V. L. Savel'ev, O. S. Artamonova, V. S. Trockaya, V. G. Vinokurov, and V. A. Zagorevski, *Khim. Heterocikl. Soedin*, **7** (1973) 885.
11. V. L. Savel'ev, N. T. Pramishnikova, O. S. Artamonova, N. Fedina, and V. A. Zagorevski, *Khim. Farm. Zh.*, **9** (1975) 10, cit. *Chem. Abstr.* **83** (1975) 188296.
12. R. G. Pearson, *J. Amer. Chem. Soc.* **85** (1963) 3533: R. G. Pearson, J. Songstad, *J. Amer. Chem. Soc.*, **89** (1967) 1827.
13. R. F. Hudson, *Chem. Eng. News*, **43** (1965) 102.
14. W. S. Trahanovsky, M. P. Doyle, *Chem. Commun.* (1967) 1021.
15. A. Kirby, T. G. Mujahid, P. Camilleri, *J. Chem. Soc. Perkin II*, (1979) 1610.
16. I. Tabaković, *Bull. Soc. Chim. (Beograd)*, **42** (1977) 761.

SAŽETAK

Elektrokemijska sinteza heterocikličkih spojeva. XI. Anelacija kumarinskog prstena pomoću katodne redukcije 3-nitrokumarinskih derivata

K. Tabaković i I. Tabaković

Anelacija kumarinskog prstena je izvršena katodnom redukcijom 3-nitrokumarinskih derivata (**1**—**4**) pri kontroliranom potencijalu. Redukcijom 3-nitro-4-aminokumarina, **1**, dobiven je 3,4-diaminokumarin, **5**. Reakcijom spoja **5** sa mravljom kiselinom dobiven je novi heterociklički sistem **6**, 4H [1] benzpirano [9,4-b] imidazol-4-on. Kondenzacijom **5** sa anhidridom octene kiseline, anhidridom trifluoroctene kiseline i benzilom dobiveni su produkti **7**, **8** i **9**.

Redukcijom 3-nitro-4-karbetoksimetiltiokumarina, **2**, dobiven je ciklički produkt **10**, 3H, 5H [1] benzpirano [3,4-b] 1,4-tiazin (2H)-3,5-dion. Redukcijom 3-nitro-4--(2-formilfenoksi)kumarina, **3**, i intramolekularnom kondenzacijom amino derivata **11** dobiven je novi heterociklički sistem **13**, 8H [1] benzpirano [3,4-b] 1,4-benzoksazepin--8 on. Isti spoj (**13**) je dobiven redukcijom 3-nitro-4-klorkumarina, **4**, u 3-amino-4--klorkumarin, **12**, i kondenzacijom spoja **12** sa salicilaldehidom.

TEHNOLOŠKI FAKULTET — BANJALUKA

Prispjelo 10. travnja 1981.