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

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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] benzopyran [3,4-b] imidazole-4-on ring system 6. The condensation of 5 with trifluoroacetic 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] benzopyran [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] benzopyran [3,4-b]1,4-benzoxazepin-8-on ring system 13. The same compound 13 was obtained through reduction of 3-nitro-4-chlorocoumarin, 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 reactivity2—6. The electrochemistry of coumarin and its derivatives has also been reviewed7. The polarographic behaviour of 3-nitro, 3-nitroso-3-phenylazo-4-hydroxycoumarin and 3-nitro-4-aminoacoumarin has been investigated recently in acid, neutral and basic solutions8.

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 molecule9.

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 a 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).
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, 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^a$ (V vs. SCE)</th>
<th>$i_a/C$ (mA M$^{-1}$)</th>
<th>n-Value$^b$</th>
<th>Potential controlled (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>-0.23</td>
<td>14</td>
<td>6.0</td>
<td>-0.50</td>
</tr>
<tr>
<td>Compound 2</td>
<td>-0.10</td>
<td>16</td>
<td>6.1</td>
<td>-0.35</td>
</tr>
<tr>
<td>Compound 3</td>
<td>-0.05</td>
<td>14</td>
<td>5.5</td>
<td>-0.50</td>
</tr>
<tr>
<td></td>
<td>-0.95</td>
<td>6</td>
<td>2.4</td>
<td>-1.05</td>
</tr>
<tr>
<td>Compound 4</td>
<td>-0.21</td>
<td>14</td>
<td>6.1</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td>-0.98</td>
<td>5</td>
<td>1.9</td>
<td>-1.05</td>
</tr>
</tbody>
</table>

*a 0.5—1 $\times 10^{-2}$ 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 $\times 10^{-2}$ 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](image)

Compound 5 was converted to 4H [1] benzopyrano [3,4-b] imidazole-4-one, 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](image)
that Pearson's\textsuperscript{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\textsuperscript{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 $\rightarrow$ 2 is an exception to the general behaviour found with other nucleophiles. However, similar exceptions are known in the literature\textsuperscript{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 cyclizes in solution giving rise to product 10. Such a conclusion is supported by the results of A. Kirby and coworkers\textsuperscript{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-one (13), outlined in Figure 4, was achieved through two different synthetic pathways.

![Figure 4](image)

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. Electrolysés 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 electrolyses were performed in the H-type cell previously described unless stated otherwise.

The cathode was a mercury pool (40 cm²) 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), and 3-nitro-4-aminocoumarin, (1), 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 recrystallization 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 (NO₂ arom.), 770 cm⁻¹; NMR (DMSO-d₆): δ = 7.5–8.5 (m, 4H arom.), 4.15 (q, 2H, CH₂), 4.1 (s, 2H, CH₂), 1.2 (t, 3H, CH₃) ppm.

Anal. for C₁₁H₁₁N₀₆S (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. Salicylaldehyde (0.53 ml, 4.4 mmol) and triethylamine (0.60 g, 4.4 mol) were added to the solution and the mixture was refluxed 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): 3290 (aldehyde CH), 1750 (aldehyde C=O), 1695 (pyrone C=O), 1605 (C=C arom.), 1530 (NO₂ arom.), 770 cm⁻¹; NMR (DMSO-d₆): δ = 10.6 (s, 1H, aldehyde CH), 8.3–7.2 (m, 3H, arom.) ppm.

Anal. for C₁₆H₉N₀₆ (311.17) calc’d: C 61.73; 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 cm²), and a graphite anode, as previously described. 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 aqueous 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%). Recrystallization from ethanol gave pure 5 with m. p. 203-205 °C. (Lit. m. p. 203-205 °C).

IR (KBr-pellet): 3360 and 3240 (NH₂), 3060 (CH arom.), 1675 (pyrone C=O), 1615 (C=C arom.), 750 cm⁻¹. NMR (DMSO-d₆): δ = 7.0-8.0 (m, 4H, arom.), 6.29 (s, 2H, NH₂), 4.16 (s, 2H, NH₂) ppm.

Anal. for C₉H₈N₂O₂ (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 the resulting crude mixture was filtered off and washed with 10 ml of 100% ethanolic HCl. Recrystallization from the mixture CH₃COOH-H₂O (1:1) gave 0.42 g (80%) of 6, m. p. 298-300 °C. IR (KBr-pellet): 3395 (NH), 3015 (CH arom.), 2940 (CH₃), 1780 (pyrone C=O), 1610 (C=C arom.), 755 cm⁻¹. NMR (DMSO-d₆): δ = 8.38 (s, 1H, CH), 7.3-8.1 (m, 5H, NH, arom.) ppm.

Anal. for C₁₀H₆N₂O₂ (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 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. The resulting precipitate of 7 was filtered off: 0.4 g (78%). Recrystallization from ethanol gave pure 7 with m. p. 335 °C. IR (KBr-pellet): 3395 (NH), 3050 (CH arom.), 2940 (CH₃), 1730 (pyrone C=O), 1610 (C=C arom.), 755 cm⁻¹. NMR (DMSO-d₆): δ = 8.72 (broad s, 1H, NH), 8.08-8.72 (m, 4H, arom.), 1.93 (s, 3H, CH₃) ppm.

Anal. for C₁₁H₇N₂O₂ (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 slowly, and upon reaching ambient temperature was poured into ice-cold water (150 ml). 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, NH₂), 1710 (pyrone C=O), 1660 (amide C=O), 1605 (C=C arom.), 755 cm⁻¹. NMR (DMSO-d₆): δ = 10.1 (broad s, 1H, NH), 8.1 (d, 2H, NH₂), 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 (24), 120 (21), 102 (13), 95 (5), 91 (8), 77 (10), 76 (78).

Anal. for C₁₁H₇N₂O₂F₃ (272.1) calc'd: C 48.54; H 2.58; N 10.28% found: C 48.32; H 2.70; N 10.82%.

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 aqueous 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 (86.0/o).

On recrystallization from ethanol, pure 9 was obtained, m. p. 204-205°C.

IR (KBr-pellet): 3060, (CH aromJ, 1745 (pyrone C=O), 1610 (C=C aromJ, 750 cm⁻¹.

NMR (DMSO-d₆): δ = 7.15-8.65 (m, 14H, arom.) ppm.

Anal. for C₂₉H₁₄N₄O₂ (350.3) calc’d: C 78.85; H 4.02; N 7.99/o.

Found: C 78.80; H 4.32; N 7.76/o.

3H, 5H [1] Benzopyranos [3,4-β] 1,4-thiazine (2H)-3,5-dione (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/o ethanol. The reduction consumed about 6 F/mole (Table I).

During electrolysis, product 10 precipitated and was separated by suction: 0.45 g (88.0/o). On recrystallization from ethanol pure 10 was obtained, m. p. 275-277°C.

IR (KBr-pellet): 3340 (NH), 2920 (CH₂), 1700 (pyrone C=O), 1670 (amide C=O), 1605 (C=C aromJ, 760 cm⁻¹.

NMR (DMSO-d₆): δ = 10.25 (broad s, 1H, NH) 7.3-7.7 (m, 4H, arom.), 3.25 (s, 2H, CH₂) ppm.

Anal. for C₁₁H₁NO₅S (233.1) calc’d: C 56.66; H 3.01; N 6.00/o.

Found: C 56.89; H 3.18; N 6.21/o.

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/o 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 (61.0/o). On recrystallization from ethanol pure 11 was obtained, m. p. 184-186°C.

IR (KBr-pellet): 3400, 3390 (NH₂), 2930 (CH aldehyde), 1805 (aldehyde C=O), 1710 (pyrone C=O), 1630 (C=C aromJ), 760 cm⁻¹.

NMR (DMSO-d₆): δ = 6.9-8.0 (m, 4H, arom.) 5.25 (broad s, 2H, NH₂) ppm.

Anal. for C₉H₆O₂Cl (195.6) calc’d: C 55.26; H 3.08; N 7.15/o.

Found: C 55.41; H 3.07; N 7.22/o.

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/o ethanol. The reduction consumed about 6 F/mole.

During electrolysis, an unidentified compound, having m. p. 270-272°C, were precipitated (~0.2 g) and were separated by suction. Most of the filtrate was evaporated in vacuo, the pH adjusted to 7-8 with NaOH, and the precipitate filtered off: 0.5 g (59.0/o).

On recrystallization from acetic acid pure 12 was obtained, m. p. 139-141°C.

IR (KBr-pellet): 3450, 3350 (NH₂), 1705 (pyrone C=O), 1630 (C=C aromJ), 755 cm⁻¹.

NMR (DMSO-d₆): δ = 6.9-8.0 (m, 4H, arom.), 5.25 (broad s, 2H, NH₂) ppm.

Anal. for C₁₄H₁₂ClO₂ (233.1) calc’d: C 55.26; H 3.08; N 7.15/o.

Found: C 55.41; H 3.07; N 7.22/o.

8H [1] Benzopyranos [3,4-β] 1,4-benzoxazepin-8-one (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 (61.0/o).

Method B. Compound 12 (0.5 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 (84.0/o) and recrystallization from cyclohexane gave pure 13 with m. p. 130-131°C.

IR (KBr-pellet): 2910, (CH) 1710 (pyrone C=O), 1610 (C=C aromJ), 760 cm⁻¹.

NMR (DMSO-d₆) δ = 8.1 (s, 1H, CH), 7.1-7.8 (m, 8H, arom) ppm. MS: m/e (relative inten-
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sity) 263 (63.5), 262 (100), 238 (21), 211 (18.5), 192 (19.2), 181 (45.2), 165 (10.6), 153 (12.9), 152 (22.1), 122 (10.6), 121 (81), 120 (12.5), 107 (74), 105 (11), 104 (12.5), 91 (18.3), 77 (31.7), 76 (41.7).

Anal. for C_{16}H_{9}N_{3}O_{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


SAZETAK

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

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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 mražljivom 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-formilfenoksijlkumarina, 3, i intramolekularnom kondenzacijom amin derivata 11 dobiven je novi heterociklički sistem 13, 8H [1] benzpirano [3,4-b] 4, benzoksazepin-8 on. Isto spoj (13) je dobiven redukcijom 3-nitro-4-klorokumarina, 4, u 3-amino-4-klorokumarin, 12, i kondenzacijom spoja 12 sa salicilaldehidom.

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