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By coupling of diazonium salts with ethyl *N*-(4-oxo-1,4-dihydroquinolin-2-yl)carbamate **4**, the corresponding 3-arylazocompounds **5** were obtained. These ones were cyclized thermally or in alkaline medium to the corresponding 2-aryl-2,3,5,10-tetrahydro-[1,2,4]triazino[5,6-*b*]quinolin-3,10-diones **6**. Compounds **6** were transformed by alkaline hydrolytic splitting to the corresponding 2-amino-3-arylazo-1,4-dihydroquinolin-4-ones **7**. Starting carbamate **4** was prepared by a two-step synthesis from 2-amino-1,4-dihydroquinolin-4-one **1**.

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The syntheses of condensed [1,2,4]triazines based on the cyclization of hydrazono-carbamates are advantageous in the cases when the starting compounds can be obtained by azo-coupling reactions with five membered aromatic heterocyclic compounds, *e.g*. at the synthesis of the pyrazolo[3,4-*e*][1,2,4]triazines [2], [1,2,4]triazinoindoles [3,4] or [1,2,4]triazines with condensed furan [5,6] or thiophene ring [7].

We were interested in the extension of the method mentioned above to be usable for a synthesis of [1,2,4]triazines with fused six membered heterocyclic ring. It is known that the reactivity of these compounds to nucleophilic attacks is much lower then that of aromatic heterocyclic compounds with a five membered ring.

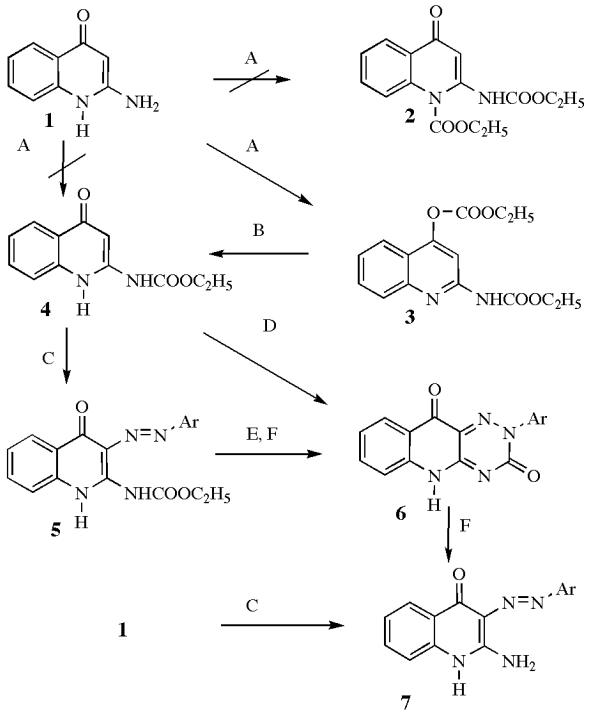
In this paper, we describe an application of this method to a quinoline system in order to investigate an alternative route for the synthesis of the little explored [1,2,4]triazino[5,6-*b*]quinoline system [8,9].

As a starting material, we chose a compound which is stated in references as 2-amino-4-hydroxyquinoline [10,11,12]. On the basis of ^{15}N NMR spectroscopy we found that this compound exists as 4-oxo-1,4-dihydroquinoline tautomer **1**. Two resonances in ^{15}N NMR spectrum of this compound [$\delta(^{15}N)$ = -261.6 (NH, broadened signal) and –310.7 (NH_2, $^1J(^{15}N, ^1H)$ = 88.8 Hz] give the evidence that the structure **1** is strongly over dominating form (compared to $\delta(^{15}N)$ = - 248 in 1-methyl-1,4-dihydropyridine-2-one [13], and to the ^{15}N chemical shift of substituted amino group at *cca.* 50 ppm [14]).

Within our effort to prepare ethyl *N*-(4-oxo-1,4-dihydroquinoline-2-yl)carbamate **4** we carried out the acylation of compound **1** with ethyl chloroformate in pyridine medium. However, direct monoacylation was unsuccessful. This fact can be explained by the formation of the tautomeric equilibrium in pyridine, where 2-amino-4-hydroxyquinoline is formed and which is more reactive at both reaction centres than tautomer **1**. Thus, the mixture of starting compound **1** and twice acylated derivative **3** was formed despite the usage of only one mol of ethyl chloroformate. Compound **3** was prepared later by acylation with the excess of ethyl chloroformate in a good yield. ^{15}N NMR spectroscopy is capable of distinguishing these forms undoubtedly. There were two signals in ^{15}N NMR spectrum of structure **3** [$\delta(^{15}N)$ = -126.2 and –263.0]). The nitrogen signal resonating at –126.2 ppm had a very similar ^{15}N chemical shift to that one in 2-aminopyridine [$\delta(^{15}N)$ = -113.8, [14]]. The nitrogen signal resonating at –263.0 ppm belonged to the NH group. These values indicate clearly that the structure **2** was not the correct structure because the $\delta(^{15}N)$ were considerably different from those in the model compounds related to structure **2**, *i.e.* in 1,4-dihydropyridine-4-one and 1-methyl-1,4-dihydropyridine-4-one, the ^{15}N chemical shift were –222 ppm and –248 ppm, respectively [12].

We found that the ethoxycarbonyl group placed in position 4 of compound **3** caused a lack of reactivity for coupling reactions, and could be easily hydrolysed contrary to

Scheme 1



the carbamate group placed in position 2. For this reason it was possible to convert compound **3** to ethyl *N*-(4-oxo-1,4-dihydroquinoline-2-yl)carbamate **4** in a good yield by boiling in aqueous ethanol – pyridine mixture.

The determination of the tautomeric form of carbamate **4** by ^{15}N NMR spectroscopy was not successful. No signals were observed. Even in ^{13}C NMR some signals were not present and some were very broad since there was probably a complicated dynamic equilibrium.

Our next interest was focused to azo coupling reactions of carbamate **4** with diazonium salts to obtain 3-arylazo derivatives **5**. These ones are suitable synthones for [1,2,4]triazino[5,6-*b*]quinoline skeleton formation.

In agreement with our hypothesis, we found that the reactivity of carbamate **4** was lower than the reactivity of analogous heterocyclic carbamates with five a membered ring [2-7]. The best yields of coupling reactions were reached in pyridine medium where carbamate **4** reacted with diazotised 4-nitroaniline resulting in 3-(4-nirophenylazo)-derivative **5c**. Lower yields were obtained with diazotised aniline and 4-bromoaniline resulting in the corresponding derivatives **5a** and **5b**. The coupling reaction of carbamate **4** with diazotised 4-methoxyaniline was unsuccessful. The yield improvement of 3-arylazoderivatives was not successful neither by the mutual change of the components ratio nor by carrying out the reaction in aqueous basic medium. It was possible to increase the yields only by the isolation of unchanged carbamate **4** after the coupling reaction and re-using it for next procedure. If the azo coupling reactions proceed in triethylamine – pyridine mixture for a long reaction time (Method D), cyclized compounds **6** were isolated.

Two resonances were found in the ^{15}N NMR spectrum of ^{15}N selectively labelled compound **5a** prepared using ^{15}N enriched aniline (96 % ^{15}N compound). The signal at –271.9 ppm belongs to the $NHCOOC_2H_5$ group while that one at 41.4 ppm can be assigned to $N\text{-}C_6H_5$ fragment and the chemical shift shows that compound **5a** exists predominantly in azo form (compared with ^{15}N chemical shifts in model azo compounds [15]). The difference in ^{15}N chemical shifts of $N\text{-}C_6H_5$ fragment in compounds **7** and **5** is negligible and it can be concluded that $NHCOOC_2H_5$ group does not influence the equilibrium as much as the amino group.

Above mentioned 2-aryl-2,3,5,10-tetrahydro[1,2,4]triazino[5,6-*b*]quinolin-3,10-diones **6** respectively their 2,3,4,10-tetrahydro tautomers were prepared in high yields by thermal cyclisation of azo-compounds **5** in boiling decalin. The lower yield was obtained by basic cyclisation of compound **5a** in hot aqueous ethanolic solution of sodium hydroxide. Prepared triazino quinolines **6** are yellow crystalline substances of high melting points, sparingly soluble in common organic solvents.

[1,2,4]Triazino[5,6-*b*]quinoline system of compounds **6** is fairy stable. Its derivatives are stable in strongly acidic medium for 24 hours. Compounds **6** are soluble in basic solutions with the formation of red coloured solutions of mesomeric anoints. After standing for 24 hours at a room temperature it was possible to recover them unchanged from these solutions. However, boiling in basic solution of sodium hydroxide led to the hydrolytic splitting of [1,2,4]triazine ring and the formation of the corresponding 2-amino-3-arylhydrazono-3,4-dihydroquinolin-4-ones, which were tautomeric with the corresponding azo derivatives **7**. These compounds were identical to compounds which had been prepared by coupling reactions of diazonium salts with 2-amino-1,4-dihydroquinolin-4-one **1**.

Sample **7** shows extremely low solubility even in hexadeuteriodimethyl sulfoxide and, thus, ^{15}N enrichment had to be used in order to determine ^{15}N chemical shifts. The ^{15}N selectively labelled compound **7a** was prepared using either ^{15}N enriched aniline (96 % ^{15}N) or ^{15}N enriched $Na^{15}NO_2$ (50 % ^{15}N). The two ^{15}N chemical shifts measured in the ^{15}N selectively labelled compound **7a** [45.4 (^{15}N enrichment from $Na^{15}NO_2$), 115.0 (^{15}N enrichment from ^{15}N-aniline)] indicate that compound **7a** exists in pure azo form [15]. The ^{15}N NMR signals of other two nitrogens were not observed due to low solubility and thus, no further conclusions could be made about other possible tautomeric equilibria.

We have attempted to prepare compound **5** from **7** by treatment of ethyl chloroformate, but the reaction was unsuccessful due to the low solubility of the compound **7**.

EXPERIMENTAL

The melting points were determined on a Boetius stage and are uncorrected. The infrared spectra were recorded in KBr wafers and scanned on an ATI Unicam Genesis FTIR instrument. Elemental analyses were performed with an EA 1108 Elemental Analyzer (Fison Instrument). ^{15}N (36.50 MHz), ^{13}C (90.56 MHz) and ^{1}H (360.13 MHz) NMR spectra were measured on a Bruker AMX 360 spectrometer equipped with 5 mm broadband probe and a Silicon Graphic Indy computer in hexadeuteriodimethyl sulfoxide at ambient temperature. The ^{13}C and ^{1}H chemical shifts were referred to the central peak of DMSO-D_6 ($\delta(^{13}C)$ = 39.60, $\delta(^{1}H)$ = 2.55). The ^{15}N chemical shifts were referred to external neat nitromethane in a co-axial capillary ($\delta(^{15}N)$ = 0.0). Positive values of chemical shifts denote high frequency shifts with respect to standards.

2-Amino-1,4-dihydroquinolin-4-one (**1**) [10,11,12].

Compound **1** has ^{1}H NMR: δ 5.56 (s,1H); 6.63 (bs,2H,NH_2); 7.21 (d,1H); 7.36 (d,1H); 7.50 (d,1H); 8.08 (d,1H); 11.4 (bs,NH,). ^{13}C NMR: δ 90.0; 116.7; 121.8; 124.7; 130.7 (all CH); 123.3; 139.0; 155.1; 175.3 (all C); ^{15}N NMR: δ -310.7 (NH_2); -261.6 (NH,bs).

Ethyl *N*-(4-Ethoxycarbonyloxyquinolin-2-yl)carbamate (**3**).

To a suspension of 2-amino-1,4-dihydroquinolin-4-one (**1**) (9.8 g, 61.2 mmol, dried at 125 °C for 3 hours) in anhydrous pyridine (150 ml), ethyl chloroformate (16 ml, 167 mmol) was added drop wise through a dropping funnel. The reaction mixture was

allowed to stand overnight at 2-5 °C. Then, it was diluted slowly with water under stirring to a total volume of 2000 ml. After standing for 5 hours, the precipitate was collected by filtration, washed with water and dried. The sample for analysis was prepared by the crystallization from ethanol. The yield 13.8 g (74.0 %), mp 126-128 °C dec. ^{1}H NMR: δ 1.30 (t, 3H, CH_3); 1.39 (t, 3H, CH_3); 4.22 (q, 2H, OCH_2); 4.40 (q, 2H, OCH_2); 7.57 (t, 1H, arom.); 7.81 (t, 1H, arom.); 7.86 (d, 1H, arom.); 7.91 (d, 1H, arom.); 8.16 (s, 1H, arom.); 10.75 (bs, 1H, NH). ^{13}C NMR: δ 14.2 and 14.4 (CH_3); 61.7 and 65.6 (OCH_2); 104.2; 121.2; 125.1; 127.7; 130.6 (all CH); 119.8; 148.0; 151.6; 152.2; 153.2; 155.8 (all C); ^{15}N NMR: δ -263.0; (NH, s); -126.2. IR (cm^{-1}): 3151, 2980, 1771, 1736, 1605, 1502, 1371, 1248, 1214, 1081, 767.

Anal. Calcd. for $C_{15}H_{16}N_2O_5$ (304.3): C, 59.21; H, 5.30; N, 9.21. Found C, 58.97; H, 5.60; N, 8.91.

Ethyl *N*-(4-Oxo-1,4-dihydroquinolin-2-yl)carbamate (**4**).

The product **3** (6.0 g; 19.7 mmol) was dissolved in a mixture of 96% ethanol (75 ml) and pyridine (20 ml). The solution was refluxed for 10 minutes, decolourised with charcoal and left to stand at a room temperature. The next day, the crystalline product was collected by suction, washed with a small amount of ethanol and dried at 125 °C for 2 hours. The yield 4.58 g (69.2 %); mp 252-254 °C dec. ^{1}H NMR: δ 1.31 (t, 3H, CH_3); 4.24 (q, 2H, OCH_2); 5.50-6.50 (bs, 1H); 7.34 (t, 1H, arom.); 7.64 (t, 1H, arom.); 7.70 (d, 1H, arom.); 8.04 (d, 1H, arom.); 10.50 (bs, 1H); 11.40 (bs, 1H). ^{13}C NMR: δ 14.4 (CH_3); 61.3 (OCH_2); 95.6; 123.1; 123.7; 131.0; 153.7. Other signals are very broad: *cca* 148.0; *cca* 122.0. IR (cm^{-1}): 3199, 3060, 2979, 1744, 1622, 1583, 1506, 1466, 1245, 1086, 757.

Anal. Calcd. for $C_{12}H_{12}N_2O_3$ (232.3): C, 62.06; H, 5.21; N, 12.06. Found C, 1.96; H, 5.30; N, 12.01.

Ethyl *N*-(3-Phenylazo-4-oxo-1,4-dihydroquinolin-2-yl)carbamate (**5a**).

A solution of aniline (186 mg, 2.00 mmol) in a mixture of ice water (12 ml) and 35% hydrochloric acid (2.6 ml) was diazotized with a solution of sodium nitrite (138 mg, 2.00 mmol) in ice water (6 ml). The mixture was stirred in an ice bath for 15 min and then added portion wise to a solution of carbamate **4** (464.6 mg, 2.00 mmol) in pyridine (50 ml), which was pre-cooled to 0–5 °C. The mixture was left to stand at 0–5 °C for 48 hours and then evaporated to dryness. The residue was mixed with water (20 ml) and this mixture was extracted with chloroform (2 x 30 ml). The chloroform extract was dried with $MgSO_4$, filtered, evaporated to dryness and dissolved again in chloroform (5 ml). Purification by elution with chloroform through a short column (4 cm i.d.) filled with silica gel 60 (230-400 mesh, 50 g) gave 120 mg (17,8 %) of orange solid; at 150 °C cyclizes to **6a** without melting. The sample for analysis was prepared by the crystallization from ethanol. ^{1}H NMR: δ 1.37 (t, 3H, CH_3); 4.35 (q, 2H, OCH_2); 7.43-7.86 (m, 8H, arom.); 8.23 (d, 1H, arom.); 11.97 (bs, 1H, NH); 13.50 (bs, 1H, NH). ^{15}N NMR: δ -271.9 (NHCOOC_2H_5); 41.4 (N-C_6H_5). IR (cm^{-1}): 3217, 3064, 2981, 1718, 1638, 1604, 1548, 1307, 1227, 764.

Anal. Calcd. for $C_{18}H_{16}N_4O_3$ (336.4): C, 64.28; H, 4.79; N, 16.66. Found C, 64.21; H, 4.65; N, 16.19.

Ethyl *N*-[3-(4-Bromophenylazo-4-oxo-1,4-dihydroquinolin-2-yl)carbamate (**5b**).

This compound was prepared in a similar way as **5a** using 4-bromoaniline (344 mg, 2.00 mmol). Yield 192.1 mg (20.4 %), at 150 °C cyclizes to **6b** without melting. IR (cm^{-1}): 3232, 2992, 1729, 1630, 1585, 1544, 1310, 1221, 770.

Anal. Calcd. for $C_{18}H_{15}N_4O_3Br$ (415.3): C, 52.07; H, 3.64; N, 13.49. Found C, 52.16; H, 3.51; N, 13.32.

Ethyl *N*-[3-(4-Nitrophenylazo-4-oxo-1,4-dihydroquinolin-2-yl)carbamate (**5c**).

A solution of 4-nitroaniline (276 mg, 2.00 mmol) in a mixture of ice water (12 ml) and 35% hydrochloric acid (2.6 ml) was diazotized with a solution of sodium nitrite (138 mg, 2.00 mmol) in ice water (6 ml). The mixture was stirred in an ice bath for 15 min and then added portion wise to a solution of carbamate **4** (464.6 mg, 2.00 mmol) in pyridine (50 ml), which was pre-cooled to 0–5 °C. The mixture was left to stand at 0–5 °C for 48 hours and then slowly diluted with ice water (60 ml). The next day the precipitated dark orange solid was collected by suction, washed with water and dried. The sample for analysis was prepared by recrystallization from a large amount of ethanol (0.6 ml per 1 mg). Yield 330.1 mg (43.3 %), at 210 °C cyclizes to **5c** without melting. IR (cm^{-1}): 3251, 2991, 1721, 1634, 1616, 1586, 1548, 1338, 1211, 753.

Anal. Calcd. for $C_{18}H_{15}N_5O_5$ (381.4): C, 56.69; H, 3.96; N, 18.38. Found C, 56.76; H, 3.79; N, 18.46.

2-Phenyl-2,3,5,10-tetrahydro[1,2,4]triazino[5,6-*b*]quinolin-3,10-diones (**6a**).

Method E.

Compound **5a** (17.5 mg, 0.052 mmol) was refluxed in decalin (3 ml) for 30 min. The mixture was cooled; the precipitated solid was collected by suction, washed with heptane and dried. The sample for analysis was prepared by crystallization from acetic acid (1 ml per 1 mg). Yield 14.1 mg (93.2 %); mp over 360 °C. ^{1}H NMR: δ 7.35 (t, 1H, arom.); 7.49 (t, 1H, arom.); 7.55-7.69 (m, 6H, arom.); 7.82 (t, 1H, arom.); 8.12 (d, 1H, arom.); 12.20 (bs, 1H, NH). IR (cm^{-1}): 3063, 1686, 1671, 1621, 1577, 1478, 1235, 802.

Anal. Calcd. for $C_{16}H_{10}N_4O_2$ (290.3): C, 66.20; H, 3.47; N, 19.30. Found C, 66.34; H, 3.56; N, 18.89.

Method F.

Compound **5a** (20.5 mg, 0.061 mmol) was dissolved in 50 % aqueous ethanolic solution (5 ml) of NaOH (about 100 mg) which resulted in a blood red solution. This solution was boiled for 1-2 min, cooled down and neutralized with diluted acetic acid. The precipitated yellow solid was collected by filtration, washed with water and dried to obtain 12.8 mg (72.3 %). Spectral data were identical to the data of the compound prepared by method E.

Method D.

A solution of aniline (186 mg, 2.00 mmol) in a mixture of ice water (8 ml) and 35% hydrochloric acid (1.2 ml) was diazotized with a solution of sodium nitrite (138 mg, 2.00 mmol) in ice water (6 ml). The mixture was stirred in an ice bath for 15 min and then added portion wise to a solution of carbamate **4** (464.6 mg, 2.00 mmol) in pyridine (50 ml) and triethylamine (5 ml), which was pre-cooled to 0–5 °C. The mixture was left to stand at 0–5 °C for 14 days. Then, the precipitated yellow compound was collected by filtration, washed with ethanol and dried. Yield 120.0 mg (27.1 %). Spectral data were identical to the data of the compound prepared by method E.

2-(4-Bromophenyl)-2,3,5,10-tetrahydro[1,2,4]triazino[5,6-*b*]-quinolin-3,10-diones (**6b**).

This compound was prepared in a similar way as compound **6a** by method A using **5b** (108.2 mg) and decalin (4 ml). Yield 94.1 mg (97.8 %), mp over 360 °C. IR (cm^{-1}): 1686, 1620, 1578, 1477, 1006, 769.

Anal. Calcd. for $C_{16}H_9N_4O_2Br$ (369.2): C, 52.06; H, 2.46, N; 15.18. Found C, 51.97; H, 2.22; N, 15.06.

2-(4-Nitrophenyl)-2,3,5,10-tetrahydro[1,2,4]triazino[5,6-*b*]-quinolin-3,10-diones (**6c**).

This compound was prepared in a similar way as compound **6a** by method A with using **5c** (165.8 mg) and decalin (6 ml). Yield 144.7 mg (99.2 %), mp over 360 °C. IR (cm^{-1}): 1697, 1673, 1622, 1578, 1527, 1476, 1350, 1299, 854.

Anal. Calcd. for $C_{16}H_9N_5O_4$ (335.3): C, 57.32; H, 2.71; N, 20.89. Found C, 57.18; H, 2.56; N, 20.68.

2-Amino-3-phenylazo-1,4-dihydroquinolin-4-one (**7a**).

Method F.

Compound **6a** (13.4 mg, 0.046 mmol) was dissolved in a solution (10 ml) of NaOH (*cca* 200 mg). This blood red colored solution was refluxed for 45 min to obtain an orange solution. Upon cooling, the mixture was neutralized with diluted acetic acid. Precipitated solid was collected by filtration, washed with water and dried. Sample for analysis was prepared by recrystallization from DMF. Yield 11.0 mg (90.1 %), mp 225-228 °C dec. ^{1}H NMR: δ 7.20 (t, 1H, arom.); 7.27-7.33 (m, 2H, arom.); 7.47 (t, 2H, arom.); 7.55 (t, 1H, arom.); 7.71 (d, 2H, arom.); 8.10 (d, 1H, arom.). ^{15}N NMR: δ 45.4; 115.0. IR (cm^{-1}): 3262, 3132, 1648, 1609, 1540, 1506, 1474, 1455, 754, 569.

Anal. Calcd. for $C_{15}H_{12}N_4O$ (264.3): C, 68.17; H, 4.58; N, 21.20. Found C, 67.91; H, 4.31; N, 20.95.

Method C.

A solution of aniline (93 mg, 1.00 mmol) in a mixture of ice water (5 ml) and 35% hydrochloric acid (0.6 ml) was diazotized with a solution of sodium nitrite (69 mg, 1.00 mmol) in ice water (2 ml). The mixture was stirred in an ice bath for 15 min and then added portion wise to a suspension of 2-amino-1,4-dihydro-quinolin-4-one (**1**) (160.2 mg, 1.00 mmol) in pyridine (40 ml), which was pre-cooled to 0–5 °C. The mixture was stirred for 5 hours and left to stand at 0–5 °C overnight. Then, the reaction mixture was diluted with ice water (150 ml). The precipitated orange solid was collected by suction, washed with water and suspended in a solution of 1 *M* NaOH (20 ml). Undissolved solid was collected again by suction, washed thoroughly with water and dried. Yield 204.3 mg (77.3 %). Spectral data were identical to the data of the compound prepared by method A

2-Amino-3-(4-bromophenylazo)-1,4-dihydroquinolin-4-one (**7b**).

This compound was prepared in a similar way as compound **7a** by method F using **6b** (57.0 mg). The sample for analysis was prepared by recrystallization from 50% acetic acid. Yield 94.1 mg (97.8 %), mp 358 °C. IR (cm^{-1}): 1651, 1612, 1512, 1476, 1340, 752.

Anal. Calcd. for $C_{15}H_{11}N_4OBr$ (343.2): C, 52.50; H, 3.23; N, 16.33. Found C, 52.62; H, 3.20; N, 16.06.

2-Amino-3-(4-nitrophenylazo)-1,4-dihydroquinolin-4-one (**7c**).

This compound was prepared in a similar way as compound **7a** by method F using **6c** (73.5 mg). The sample for analysis was prepared by recrystallization from 50 % acetic acid. Yield 62.2 mg (91.7 %), mp over 360 °C. IR (cm^{-1}): 1654, 1615, 1519, 1477, 1328, 750.

Anal. Calcd. for $C_{15}H_{11}N_5O_3$ (309.3): C, 58.25; H, 3.58; N, 22.64. Found C, 58.34; H, 3.40; N, 22.42.

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