

SYNTHESIS OF SOME DERIVATIVES
OF 1,2,4-TRIAZINO[2,3-*a*]BENZIMIDAZOLE*

J. SLOUKA

*Department of Analytical and Organic Chemistry,
Palacký University, 771 46 Olomouc*

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Coupling of ethyl cyanoacetylcarbamate or cyanoacetamide with diazonium salts afforded hydrazones *I*–*III*. The hydrazones *I* and *III* were cyclised to the corresponding 2-aryl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitriles *IV* and *V*. Reduction of the nitro group gave 2-(*o*-aminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-6-carbonitrile (*VI*) which was hydrolysed to the corresponding acid *IX*. The acid *IX* was also obtained by reduction of the 2-(*o*-nitrophenyl) acid *VIII*. The triazine *VI* was cyclised to the corresponding 3-oxo-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazole-2-carbonitrile (*X*). This was saponified to the acid *XI* which was obtained also by the cyclisation of the amino acid *IX*. The nitrile *X* was transformed into the amidoxime *XII* and further to the 1,2,4-oxadiazolyl derivative *XIII*.

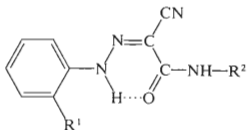
Contrary to their [4,5-*a*] (ref.^{1–9}) and [3,4-*a*] (ref.^{10–12}) isomers, 1,2,4-triazino[2,3-*a*]benzimidazoles have received only little attention. A small number of known derivatives of this heterocyclic system was prepared by condensation of 1,2-diaminobenzimidazole with α -dicarbonyl compounds¹³. This communication describes an alternative route leading to compounds of this type which is based on the formation of the benzimidazole ring in 2-(*o*-aminophenyl)-2,3,4,5-tetrahydro-1,2,4-triazine-3,5-dione derivatives. As expected, these cyclisations were facile, similarly to the already described¹⁴ analogous cyclisations of 2-(*o*-carbamoyl) derivatives.

The starting compounds for the present synthesis, ethyl *o*-nitrophenylhydrazonocynoacetylcarbamate (*I*) and the *o*-phthalimidophenyl derivative *III*, were obtained in high yield by coupling of the corresponding diazonium salts with ethyl cyanoacetylcarbamate. Alkaline or thermal cyclisation of the hydrazones *I* and *III* afforded the corresponding *o*-substituted 2-phenyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitriles *IV* and *V*.

In accord with the previous results^{15,16}, the triazine *IV* undergoes a facile hydrolytic ring opening to *o*-nitrophenylhydrazonocynoacetamide (*II*). The ring fission proceeds smoothly prolonged boiling in aqueous pyridine. For comparison, the hydrazone *II* was prepared also by coupling of cyanoacetamide with an *o*-nitrobenzene-

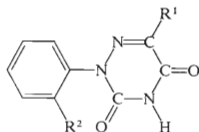
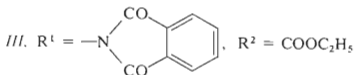
* Part XXII in the series 1-Aryl-6-azauracils; Part XXI: Acta Univ. Palacki. Olomuc., Fac. Rerum Natur. 49, 215 (1976).

diazonium salt. In an acid medium the triazine ring of the nitrile *IV* is more stable and it was therefore possible to hydrolyse this compound to 2-(*o*-nitrophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carboxylic acid (*VIII*) by boiling with hydrochloric acid.

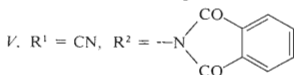


I. $R^1 = \text{NO}_2$, $R^2 = \text{COOC}_2\text{H}_5$

II. $R^1 = \text{NO}_2$, $R^2 = \text{H}$



IV. $R^1 = \text{CN}$, $R^2 = \text{NO}_2$



VI. $R^1 = \text{CN}$, $R^2 = \text{NH}_2$

VII. $R^1 = \text{CN}$, $R^2 = \text{NH}-\text{CO}-\text{CH}_3$

VIII. $R^1 = \text{COOH}$, $R^2 = \text{NO}_2$

IX. $R^1 = \text{COOH}$, $R^2 = \text{NH}_2$

Reduction of the triazine *IV* to 2-(*o*-aminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitrile (*VI*) was accomplished only by the action of iron(II) hydroxide. Metal reduction in an acid medium led to simultaneous hydrolysis of the nitrile group, catalytic reduction attacked also the 1,2,4-triazine ring. Acid hydrolysis of the nitrile *VI* afforded 2-(*o*-aminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carboxylic acid (*IX*). This acid was obtained also by Béchamp reduction of the nitro acid *VIII* and by the total saponification of the phthalimido nitrile *V*. Cyclisation of the *o*-aminophenyl derivatives *VI* and *IX* to the 2-substituted 3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazol-3-ones *X* and *XI* was effected by heating above their melting point as well as by boiling in acetic acid or nitrobenzene. The cyclisation of the nitrile *VI* by boiling in acetic acid was accompanied by formation of the acetylamino derivative *VII* which was obtained also by acetylation of the triazine *VI* with acetic anhydride. 3-Oxo-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazole-2-carboxylic acid (*XI*) was obtained by cyclisation of the amino acid *IX* or by acid hydrolysis of the nitrile *X*. Addition of hydroxylamine to the nitrile *X* led to the corresponding amidoxime *XII* which was cyclised in boiling acetic anhydride to 2-(5-methyl-1,2,4-oxadiazol-3-yl)-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazol-3-one (*XIII*).

Besides in the mentioned 3,4-dihydro tautomeric form, all the prepared 1,2,4-triazino[2,3-*a*]benzimidazole derivatives can exist also as the 3,5-dihydro tautomers. They are weak N-acids which are a little stronger than 6-azaauracils; the triazine *X*

has pK_a 5.32. The 1,2,4-triazino[2,3-*a*]benzimidazole system resists considerably to hydrolytic cleavage, as shown by the fact that boiling the triazine *X* in hydrochloric acid results only in hydrolysis of the nitrile group. On the contrary, hydrolysis of the triazines *V* or *VI* with boiling hydrochloric acid is accompanied to a small extent by closure of the benzimidazole ring (formation of the acid *XI*).



X, R = CN

XI, R = COOH

XII, R = $\begin{array}{l} \text{NOH} \\ \text{C} \\ \text{NH}_2 \end{array}$

XIII, R = $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{C}-\text{CH}_3 \\ \diagup \quad \diagdown \\ \text{N} \end{array}$

Infrared spectra of all the prepared compounds exhibit carbonyl bands at about 1700 cm^{-1} . These bands are very strong in the spectra of the compounds *I*–*IX*, but they are much weaker in the spectra of compounds with condensed rings (*X* to *XIII*). The bands of the CN groups, situated in the spectra of the hydrazones *I*–*III* at about 2200 cm^{-1} , are shifted in the spectra of the triazines *IV*–*VI* and *X* to higher wavenumbers (above 2240 cm^{-1}).

EXPERIMENTAL

The melting points were determined on a Boetius apparatus and are uncorrected. IR spectra were measured in nujol mull on a UR-20 (Zeiss, Jena) spectrophotometer. UV spectra were taken on a Unicam SP 1800 instrument in $5.0 \cdot 10^{-4}\text{M}$ solutions in 50% ethanol.

Ethyl *o*-Nitrophenylhydrazonocynoacetylcarbamate (*I*)

Hydrochloric acid (37%, 15 ml) was added to a solution of *o*-nitroaniline (2.80 g; 20.27 mmol) in acetic acid (30 ml). A solution of NaNO_2 (1.40 g; 20.3 mmol) in ice-cold water (5 ml) was added at 0 – 5°C and the thus-obtained solution of the diazonium salt was added portionwise under stirring to a pre-cooled solution of ethyl cyanoacetylcarbamate (4.2 g; 26.9 mmol) and sodium acetate trihydrate (50 g) in water (900 ml). After 2 hours the separated yellow compound was filtered, thoroughly washed with water and dried; yield 5.95 g (96.2%), m.p. 181 – 183°C (ethanol).

IR spectrum (nujol, cm^{-1}): 746 m, 775 m, 790 m, 834 w, 760 m, 785 m, 924 s, 955 w, 1020 s, 1132 s, 1145 s, 1181 s, 1450 m, 1485 s, 1525 sh, 1557 w, 1591 m, 1615 m, 1708 m, 1755 sh, 1787 s, 2220 m, 3235 m, 3410 m. For $\text{C}_{12}\text{H}_{11}\text{N}_5\text{O}_5$ (305.3) calculated: 47.21% C, 3.63% H, 22.95% N; found: 47.40% C, 3.81% H, 23.00% N.

o-Nitrophenylhydrazonocynoacetamide (II)

a) *By coupling*: A solution of *o*-nitrobenzenediazonium chloride, prepared from *o*-nitroaniline (2.80 g; 20.3 mmol) in the same manner as described in the above experiment, was added in portions to a stirred solution of cyanoacetamide (3.40 g; 40.4 mmol) and sodium acetate (60 g) in ice-cold water (200 ml). After several hours the yellow compound was filtered, washed with water and dried; yield 4.65 g (98.4%), m.p. 232–234°C (ethanol). IR spectrum (nujol, cm^{-1}): 740 s, 780 m, 792 m, 863 m, 887 w, 963 w, 1048 sh, 1076 m, 1140 sh, 1155 s, 1200 s, 1290 sh, 1320 s, 1330 s, 1385 sh, 1405 s, 1455 m, 1485 sh, 1503 s, 1523 s, 1545 sh, 1590 m, 1610 s, 1708 s, 2215 m, 3290 m, 3455 m. For $\text{C}_9\text{H}_7\text{N}_5\text{O}_3$ (233.2) calculated: 46.35% C, 3.03% H, 30.04% N; found: 46.61% C, 3.16% H, 29.93% N.

b) *By cleavage of the triazine IV*: A mixture of the triazine IV (260 mg; 1.00 mmol), water (25 ml) and pyridine (1.5 ml) was refluxed for 100 h. After cooling, the yellow needles were filtered, washed with water and dried; yield 155 mg (66.3%). Crystallisation from acetic acid afforded a product which was identical with the compound prepared by the method a).

Ethyl *o*-Phthalimidophenylhydrazonocynoacetylcarbamate (III)

A mixture of *o*-phthalimidoaniline¹⁷ (2.38 g; 10.0 mmol), acetic acid (75 ml) and 37% HCl (7.5 ml) was cooled in an ice bath, crushed ice (10 g) was added and the mixture was diazotised by addition of NaNO_2 (690 mg; 10.0 mmol) in ice-cold water (10 ml). The suspension dissolved during the addition. The resulting solution was stirred for 20 minutes in an ice bath and then added portionwise to a stirred solution of ethyl cyanoacetylcarbamate (2.10 g; 13.4 mmol) and sodium acetate (30 g) in ice-cold water (450 ml) to which crushed ice was added. The mixture was set aside at 0–5°C overnight. The yellow compound was filtered, washed with water and dried, yielding 3.62 g (89.4%) of the product melting at 190–192°C (ethanol). IR spectrum (nujol, cm^{-1}): 717 s, 739 m, 755 s, 785 w, 791 w, 802 w, 838 w, 858 m, 880 m, 927 s, 1000 m, 1028 s, 1075 m, 1113 s, 1131 s, 1158 s, 1185 s, 1235 m, 1284 s, 1343 sh, 1374 s, 1435 sh, 1450 m, 1490 s, 1551 s, 1605 m, 1689 sh, 1712 s, 1772 s, 2221 m, 3149 w, 3215 sh, 3265 m, 3315 m. For $\text{C}_{20}\text{H}_{15}\text{N}_5\text{O}_5$ (405.4) calculated: 59.26% C, 3.73% H, 17.28% N; found: 59.51% C, 3.69% H, 17.26% N.

2-(*o*-Nitrophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitrile (IV)

A mixture of the hydrazone I (3.06 g; 10.0 mmol), NaCO_3 (2.12 g) and water (150 ml) was allowed to stand at room temperature with intermittent stirring for 10 days, then filtered and acidified (pH 1). Next day the separated compound was filtered, washed with water and dried, yield 2.19 g (84.3%), m.p. 229–231°C (toluene). IR spectrum (nujol, cm^{-1}): 710 s, 720 sh, 751 m, 775 m, 783 sh, 794 m, 808 w, 861 w, 880 sh, 890 w, 969 w, 1016 m, 1040 sh, 1145 w, 1168 m, 1192 s, 1253 m, 1274 m, 1303 sh, 1317 m, 1335 s, 1349 s, 1403 m, 1428 s, 1455 m, 1470 m, 1485 m, 1535 s, 1449 m, 1590 m, 1610 m, 1690 sh, 1724 s, 1743 s, 1845 w, 2254 m, 3125 m, 3235 s. For $\text{C}_{10}\text{H}_5\text{N}_5\text{O}_4$ (259.2) calculated: 46.34% C, 1.94% H, 27.02% N; found: 46.53% C, 1.98% H, 27.19% N.

2-(*o*-Phthalimidophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitrile (V)

A mixture of the hydrazone *III* (1.62 g; 40.0 mmol) and xylene (80 ml) was refluxed for 24 h. After cooling the separated compound was filtered, washed with benzene and dried; yield 1.26 g (87.7%), m.p. 261–262°C (toluene). IR spectrum (nujol, cm^{-1}): 710 m, 720 s, 742 w, 766 m, 798 w, 854 w, 893 m, 1016 m, 1500 sh, 1087 m, 1115 m, 1150 sh, 1187 s, 1223 s, 1255 m, 1277 m, 1300 m, 1325 s, 1373 sh, 1388 s, 1425 m, 1450 sh, 1503 s, 1550 m, 1608 s, 1712 s, 1725 sh, 1753 s, 1790 m, 2248 m, 3080 m, 3185 m. For $\text{C}_{18}\text{H}_9\text{N}_5\text{O}_4$ (359.3) calculated: 60.17% C, 2.52% H, 19.49% N; found: 60.40% C, 2.65% H, 19.61% N.

2-(*o*-Aminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitrile (VI)

A solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (10.5 g; 37.8 mmol) in water (50 ml) was added to a solution of the triazine *IV* (1.30 g; 5.02 mmol) in a mixture of water (40 ml) and 25% ammonia solution (0.5 ml). The reaction mixture was heated on a steam bath and 25% ammonia (9 ml) was added portionwise under stirring in the course of 10 minutes. After heating and stirring for further 30 minutes, the mixture was filtered and the precipitate washed thoroughly on the filter with hot water. The combined filtrates were taken down *in vacuo* and the residue was dissolved in hot water (30 ml) and treated with charcoal. The solution was filtered, acidified with acetic acid (pH 5) and cooled. Next day, the separated yellow compound was filtered, washed with ice-cold water and dried, yield 670 mg (58.3%). Upon crystallisation from water, the product melted at 221–223°C and then solidified again. Concentration of the mother liquors afforded further portion of less pure compound. IR spectrum (nujol, cm^{-1}): 730 w, 744 sh, 753 s, 766 m, 799 w, 864 w, 900 w, 942 w, 1019 m, 1050 m, 1078 w, 1150 sh, 1161 m, 1185 s, 1255 m, 1275 m, 1320 sh, 1328 s, 1360 sh, 1404 s, 1455 m, 1530 s, 1548 sh, 1575 sh, 1590 s, 1632 m, 1680 sh, 1710 s, 1725 sh, 2244 m, 3320 m, 3395 m. For $\text{C}_{10}\text{H}_7\text{N}_5\text{O}_2$ (229.2) calculated: 52.40% C, 3.08% H, 30.56% N; found: 52.42% C, 3.17% H, 30.60% N.

2-(*o*-Acetylaminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carbonitrile (VII)

A mixture of the triazine *VI* (115 mg; 0.50 mmol) and acetic anhydride (1.5 ml) was shortly refluxed, poured into water (10 ml) and taken down. The residue was crystallised from water, yielding 105 mg (77.2%) of the product, m.p. 308–310°C. For $\text{C}_{12}\text{H}_9\text{N}_5\text{O}_3$ (271.2) calculated: 53.14% C, 3.34% H, 25.82% N; found: 52.94% C, 3.32% H, 26.06% N.

2-(*o*-Nitrophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carboxylic Acid (VIII)

A mixture of the nitrile *IV* (520 mg; 2.01 mmol), 37% HCl (10 ml) and water (5 ml) was refluxed for 4 hours and then taken down *in vacuo*. Crystallisation of the residue from a small volume of water afforded 480 mg (80.8%) of the monohydrate, m.p. 213–214°C. For $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_6 \cdot \text{H}_2\text{O}$ (296.2) calculated: 40.55% C, 2.72% H, 18.92% N; found: 40.69% C, 2.66% H, 19.02% N. The loss of weight after drying at 110°C corresponded to 1 molecule of crystal water. IR spectrum (nujol, cm^{-1}): 710 s, 743 m, 753 m, 760 sh, 786 s, 810 s, 815 s, 865 m, 880 w, 965 w, 1023 m, 1035 w, 1052 m, 1100 s, 1105 sh, 1148 s, 1172 s, 1178 sh, 1227 s, 1277 m, 1300 sh, 1311 s, 1330 s, 1360 s, 1383 m, 1392 m, 1421 s, 1475 sh, 1492 m, 1521 s, 1568 m, 1592 m, 1622 m, 1716 sh, 1723 s, 1762 s, 3220 s, 3453 m, 3611 m. For $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_6$ (278.2) calculated: 43.17% C, 2.17% H, 20.14% N; found: 42.95% C, 2.29% H, 20.18% N.

2-(*o*-Aminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazine-6-carboxylic Acid (*IX*)

a) *By saponification of the nitrile VI*: A mixture of the nitrile *VI* (230 mg; 1.00 mmol), 37% HCl (6 ml) and water (3 ml) was refluxed for 4 h, cooled and the separated crystalline solid (15 mg) was filtered, washed with water and crystallised from water. It was identical in all respects with the acid *XI*. The filtrate was taken down *in vacuo*, a small amount of water was added to the residue and the pH was adjusted to 4 by addition of ammonia. The separated acid *IX* was filtered, washed with ice-cold water and dried at 110°C, yield 210 mg (78.9%), m.p. 240–242°C (water). IR spectrum (nujol, cm^{-1}): 728 s, 743 m, 762 s, 788 w, 814 sh, 820 m, 860 m, 865 sh, 957 w, 1028 m, 1046 w, 1126 m, 1145 sh, 1152 s, 1183 m, 1212 m, 1236 w, 1272 m, 1313 s, 1322 s, 1393 s, 1420 s, 1448 s, 1470 sh, 1506 s, 1540 sh, 1555 sh, 1575 sh, 1594 s, 1685 sh, 1695 s, 1731 s. For $\text{C}_{10}\text{H}_8\text{N}_4\text{O}_4$ (248.2) calculated: 48.39% C, 3.25% H, 22.58% N; found: 48.31% C, 3.26% H, 22.36% N.

b) *By saponification of the nitrile V*: A mixture of the nitrile *V* (360 mg; 1.00 mmol), 37% HCl (25 ml) and water (15 ml) was refluxed for 15 h and taken down. The residue was extracted by cold 3% hydrochloric acid (2×5 ml), the extract was washed several times with ether and taken down. The residue was worked up as described under a); yield 186 mg (74.8%). Crystallisation from water afforded a product which was identical with the compound obtained by saponification of the nitrile *VI*.

c) *By reduction of the acid VIII*: Hydrochloric acid (37%; 0.1 ml) was added to a boiling solution of monohydrate of the acid *VIII* (300 mg; 1.01 mmol) in water (40 ml). To the stirred solution iron powder (400 mg; 7.16 mmol) was added in the course of 2 hours and the mixture was stirred and heated on a steam bath for 3 h. After addition of 25% ammonia (1 ml) the mixture was filtered, the precipitate washed on the filter with boiling water and the filtrates were taken down. The residue was dissolved in water (15 ml), the solution treated with charcoal, filtered and concentrated to a small volume. The pH of the solution was adjusted to 3–4 by addition of hydrochloric acid. Upon cooling, the crystalline compound was filtered, washed with ice-cold water and dried at 110°C, yield 165 mg (65.6%). Crystallisation from water afforded a compound identical with the products of the preceding procedures.

3-Oxo-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazole-2-carbonitrile (*X*)

a) *By fusion of the triazine VI*: The nitrile *VI* (230 mg; 1.00 mmol) was heated to 250°C till the decomposition ceased and the originally formed melt solidified. Crystallisation from acetic acid (charcoal) afforded 175 mg (80.5%) of yellow crystals, melting above 360°C. IR spectrum (nujol, cm^{-1}): 712 m, 722 m, 739 m, 766 s, 780 m, 830 w, 873 w, 898 w, 951 w, 1011 m, 1052 m, 1075 sh, 1106 m, 1157 s, 1170 sh, 1186 m, 1215 sh, 1246 m, 1273 m, 1316 m, 1330 m, 1359 s, 1386 s, 1430 s, 1450 s, 1488 s, 1503 s, 1540 sh, 1555 sh, 1568 s, 1582 s, 1600 sh, 1628 m, 1670 m, 2242 m. UV spectrum (ethanol) λ_{max} (log ϵ): 214 nm (4.51), 265 nm (4.54), 279 nm (4.58), 286 nm (4.60), 343 nm (3.96). $\text{p}K_{\text{a}}$ 5.32 ± 0.02 (measured spectrophotometrically in 50% aqueous ethanol, ionic strength 0.05, concentration $5.0 \cdot 10^{-4}$ M, wavelength 390 nm). For $\text{C}_{11}\text{H}_5\text{N}_5\text{O}$ (211.2) calculated: 56.87% C, 2.39% H, 33.17% N; found: 56.79% C, 2.59% H, 33.32% N.

b) *By boiling in acetic acid*: A solution of the nitrile *VI* (230 mg; 1.00 mmol) in acetic acid (20 ml) was refluxed for 10 h. After cooling, the yellow compound was filtered, washed with acetic acid and dried at 130°C, yield 150 mg (70.8%), m.p. above 360°C. UV and IR spectra are identical with those of the compound prepared by the procedure a). Concentration of the mother liquor to a small volume afforded 35 mg of the triazine *VII*.

3-Oxo-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazole-2-carboxylic Acid (*XI*)

a) *By hydrolysis of the nitrile X*: A mixture of the nitrile *X* (215 mg; 1.02 mmol), 37% HCl (55 ml) and water (27 ml) was refluxed for 4 h, taken down and the residue crystallised from water. Upon cooling, the solution deposited 165 mg (70.4%) of a crystalline compound which decomposed at 260–265°C but did not melt below 360°C. IR spectrum (nujol, cm^{-1}): 698 m, 723 m, 745 w, 767 s, 789 m, 820 m, 883 w, 953 w, 977 w, 1008 w, 1073 w, 1106 m, 1132 m, 1155 w, 1172 m, 1190 m, 1235 w, 1308 s, 1381 s, 1450 s, 1470 sh, 1495 sh, 1540 w, 1583 m, 1615 m, 1640 m, 1714 m, 1732 m. For $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_3$ (230.2) calculated: 52.18% C, 2.63% H, 24.34% N; found: 52.42% C, 2.72% H, 24.56% N.

b) *By cyclisation of the acid IX*: A mixture of the acid *IX* (250 mg; 1.01 mmol) and acetic acid (125 ml) was refluxed for 10 h and concentrated to 40 ml. Upon cooling, the mixture afforded 175 mg (75.5%) of a crystalline compound which, after crystallisation from water, was identical with the acid prepared by the method a).

3-Oxo-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazole-2-carboxylic Acid Amidoxime (*XII*)

Hydroxylamine hydrochloride (100 mg; 1.44 mmol) was added to a solution of the nitrile *X* (110 mg; 0.52 mmol) in a mixture of water (10 ml) and 25% aqueous ammonia (2 ml). The mixture was set aside for 4 days at room temperature and then acidified with acetic acid. The yellow precipitate was filtered, washed with water and dried, yield 125 mg (98.3%), m.p. (decomposition) 293–295°C (ethanol). IR spectrum (nujol, cm^{-1}): 711 w, 728 m, 740 sh, 756 s, 785 w, 804 m, 856 m, 888 w, 960 s, 1008 w, 1111 w, 1140 m, 1155 sh, 1188 w, 1225 w, 1249 m, 1321 m, 1347 w, 1382 m, 1423 s, 1449 s, 1470 sh, 1490 sh, 1508 sh, 1519 s, 1558 sh, 1578 s, 1616 s, 1638 s, 1705 w, 3365 s, 3465 m. For $\text{C}_{10}\text{H}_8\text{N}_6\text{O}_2$ (244.2) calculated: 49.18% C, 3.30% H, 34.42% N; found: 49.10% C, 3.36% H, 34.70% N.

2-(5-Methyl-1,2,4-oxadiazol-3-yl)-3,4-dihydro-1,2,4-triazino[2,3-*a*]benzimidazol-3-one (*XIII*)

A mixture of the amidoxime *XII* (125 mg; 0.51 mmol), acetic acid (40 ml) and acetic anhydride (10 ml) was refluxed for 4 h, concentrated to about 10 ml and diluted with water (30 ml). Next day the separated compound was filtered, washed with water and dried, yield 105 mg (76.5%), m.p. 345–347°C (water). IR spectrum (nujol, cm^{-1}): 705 m, 724 m, 736 m, 753 s, 780 m, 793 m, 803 w, 832 w, 850 w, 883 m, 900 w, 938 w, 956 w, 980 w, 1008 w, 1032 w, 1057 w, 1102 m, 1112 m, 1163 w, 1231 m, 1258 m, 1293 w, 1320 w, 1345 w, 1385 s, 1404 m, 1443 s, 1479 m, 1540 m, 1583 s, 1619 s, 1643 s, 1699 w. For $\text{C}_{12}\text{H}_8\text{N}_6\text{O}_2$ (268.2) calculated: 53.73% C, 3.01% H, 31.33% N; found: 53.57% C, 3.24% H, 31.34% N.

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REFERENCES

1. Slouka J.: *Tetrahedron Lett.* 1968, 4007.
2. Pankina Z. A., Shchukina M. N.: *Khim. Geterotsikl. Soedin.* 1968, 830.
3. Slouka J.: *Monatsh. Chem.* 100, 91 (1969).
4. Finch N., Gemenden Ch. W.: *Tetrahedron Lett.* 1969, 1203.
5. Pankina Z. A., Shchukina M. N.: *Khim.-Farm. Zh.* 3, 15 (1969).

6. Pankina Z. A., Shchukina M. N.: *Khim. Geterotsikl. Soedin.* 1970, 245.
7. Finch N., Gemenden Ch. W.: *J. Org. Chem.* 35, 3114 (1970).
8. Pankina Z. A., Shchukina M. N., Kostyuchenko N. P., Sheinker Yu. N.: *Khim.-Farm. Zh.* 4, 12 (1970).
9. Slouka J., Peč P., Urbanová J.: *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.* 37, 481 (1972).
10. Kochergin P. M., Povstyanoi N. N.: *Khim. Geterotsikl. Soedin.* 1970, 573.
11. Kochergin P. M., Povstyanoi N. N.: U.S.S.R. 384 821; *Chem. Abstr.* 79, 105299 (1973).
12. Kolodyazhnaya S. N., Simonov A. M., Zheltikova N. N., Pozharskii A. F.: *Khim. Geterotsikl. Soedin.* 1973, 714.
13. I-Fu Ho R., Day A. R.: *J. Org. Chem.* 38, 3084 (1973).
14. Slouka J., Bekárek V.: *J. Prakt. Chem.* 316, 943 (1974).
15. Slouka J.: *Monatsh. Chem.* 100, 342 (1969).
16. Slouka J., Budiková M.: *Acta Univ. Palacki. Olomuc., Fac. Rerum Natur.* 45, 113 (1974).
17. Rupe H., Thiess K. G.: *Ber. Deut. Chem. Ges.* 42, 4287 (1909).

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