Synthesis of *as*-Triazino[5,6-*b*]quinoline, a New Heterocyclic Ring System

István Hajpál and Edit Berényi*,

EGYT Pharmacochemical Works, Budapest, Hungary

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The first representatives of a new ring system, 3-oxo-2,3,4,10-tetrahydro-*as*-triazino[5,6-*b*]quinoline and some of its derivatives were synthesized by cyclization of the appropriate (2-aminobenzyl)-triazines. These substances are in equilibrium with the tautomer 1,2,3,4-tetrahydro form.

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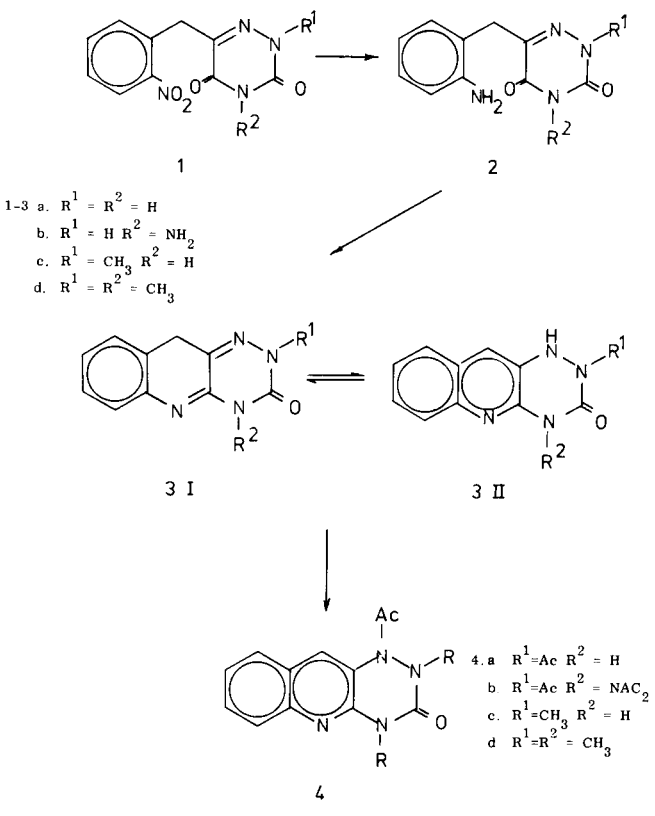
Ten isomer structures can be drawn of the *as*-triazinoquinolines containing no nitrogen atom at the site of anellation. Out of these, only *as*-triazino[5,6-*c*]quinoline and *as*-triazino[6,5-*c*]quinoline are known (1,2,3). In the course of this work, some representatives of the hitherto unknown *as*-triazino[5,6-*b*]quinoline ring system have been prepared. (2-Nitrobenzyl)triazines (**1a-d**) were reduced to the amine derivatives (**2a-d**) by catalytic reduction in a good yield. The desired structures **3a-d** were then obtained by forming the pyridine ring through dehydration of **2a-d**. On the basis of the thermoanalysis performed on **2a**, the loss of water began at 190°, however, the substances obtained by heat treatment were not pure enough. The cyclization could be carried out in a good yield by catalysis with acetic acid and the purity of the substances obtained in this way was satisfying. (Scheme).

SCHEME



The structure of the new ring system was proved by ir and nmr studies. Two tautomeric forms of the compounds **3a-d** were possible and in the case of **3d** both forms could be shown by spectroscopy. No band indicating the presence of an NH group appeared in the ir spectrum taken up in solid phase, a fact supporting the tautomeric form I, while the signal of the NH proton was found in the nmr spectrum prepared in DMSO-d_6 and a single proton was shown on the carbon atom 10, and observation proving the tautomeric form II.

On acetylation all the four compounds **3a-d** reacted in the form II, *i.e.*, as 1,2,3,4-tetrahydro tautomers.

The sites of the acetyl groups were investigated by spectroscopical methods. The acetylation at nitrogen 1 was proved by shift of the single proton at the carbon 10. As a monoacetyl derivative **4c** was only formed from **3c** and thus, no acetylation occurred at nitrogen 4, the 1,2-diacetyl structure of **4a** has been rendered likely.

EXPERIMENTAL

General Method for the Preparation of 6-(2-Aminobenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-*as*-triazines (**2a-d**).

A solution of **1a-d** (0.1 mmole) in ethanol (800 ml) was hydrogenated in the presence of a palladium-on-carbon catalyst until the consumption of hydrogen ceased. The suspension was heated to boiling and the catalyst was filtered out. On cooling the product precipitated. The data are contained in Table A.

General Method for the Preparation of 3-Oxo-2,3,4,10-tetrahydro-*as*-triazino[5,6-*b*]quinolines (**3a-d**).

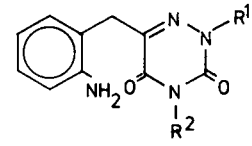
A solution of **2a-d** (0.1 mole) in the mixture of water, acetic acid and ethanol was boiled for 1 hour; then cooled and the crystals precipitated were filtered. The data are shown in Table B.

General Method for the Preparation of the Acetyl Derivatives **4a-d** of 3-Oxo-1,2,3,4-tetrahydro-*as*-triazino[5,6-*b*]quinolines.

A solution of **3a-d** (0.1 mole) in acetic anhydride or in the mixture of acetic anhydride with pyridine was boiled. Sometimes the product crystallized out, in some cases it was obtained after pouring the reaction mixture into water. The data are found in Table C.

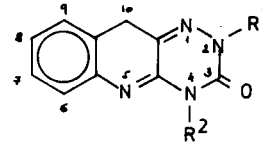
The melting points are uncorrected. The ir spectra were obtained in potassium bromide on a Perkin-Elmer spectrometer. The nmr spectra were taken up in DMSO-d_6 on a Hitachi Perkin Elmer R 24A 60 mHz device. Chemical shifts were measured in ppm (δ) with respect to TMS.

Table A



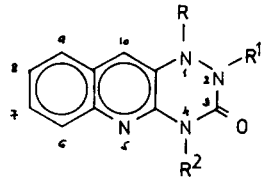
Compound	R^1	R^2	Yield %	Mp °C	Formula Mol. wt.	Analysis Calcd./Found C	H	N	IR Spectral Data cm^{-1}
a	H	H	93.4	230-232	$C_{10}H_{10}N_4O_2$	55.04	4.62	25.68	1720, 1670
					218.21	54.89	4.84	25.76	(C=O)
b	H	NH_2	84.5	178-179	$C_{10}H_{11}N_5O_2$	51.50	4.75	30.03	1730, 1675
					233.23	51.51	4.85	29.84	(C=O)
c	CH_3	H	69.8	195-197	$C_{11}H_{12}N_4O_2$	56.87	5.21	24.13	1715, 1690,
					232.24	57.06	5.24	24.08	1670 (C=O)
d	CH_3	CH_3	71.5	157-158	$C_{12}H_{14}N_4O_2$	58.52	5.73	22.75	1710, 1660
					246.26	58.82	5.80	22.90	(C=O)

Table B



Compound	R^1	R^2	Solvent	Yield %	Mp °C	Formula Mol. wt.	Analysis Calcd./Found C	H	N	IR Data cm^{-1}	NMR Spectral Data
a	H	H	H_2O (200 ml) AcOH (100 ml) EtOH (100 ml)	82.5	259-261	$C_{10}H_8N_4O$ 200.14	59.99 59.80	4.03 4.04	27.99 27.78	1670 (C=O)	4.05 (s, 2, CH_2), 6.9-7.5 (m, 4, Ar-H), 10.5 (s, 1, NH); 12.0 (s, 1, NH)
b	H	NH_2	H_2O (120 ml) AcOH (20 ml) EtOH (120 ml)	92.2	237-240	$C_{10}H_9N_5O$ 214.12	55.81 55.91	4.21 4.32	32.54 32.45	1695 (C=O)	
c	CH_3	H	H_2O (150 ml) AcOH (25 ml) EtOH (150 ml)	92.9	290-292	$C_{11}H_{10}N_4O$ 214.22	61.67 61.94	4.71 4.90	26.15 26.30	1650 (C=O)	3.55 (s, 3, CH_3), 4.05 (s, 2, CH_2), 6.9-7.25 (m, 4, Ar-H), 10.65 (s, 1, NH)
d	CH_3	CH_3	AcOH (25 ml)	91.5	160-161	$C_{12}H_{12}N_4O$ 228.25	63.14 62.95	5.30 5.41	24.55 24.44	1690 (C=O) no NH bands!	3.1 (s, 3, CH_3), 3.4 (s, 3, CH_3), 7.1-7.75 (m, 5, Ar-H), 8.05 (s, 1, NH)

Table C



Compound	R	R^1	R^2	Solvent	Yield %	Mp °C	Formula Mol. wt.	Analysis Calcd./Found C	H	N	IR cm^{-1}	NMR Spectral Data δ, ppm
a	Ac	Ac	H	Ac_2O	88.8	247-248	$C_{14}H_{12}N_4O_3$ 284.27	59.15 58.96	4.26 4.33	19.71 19.62	1730 (C=O)	2.2 (s, 3, CH_3), 2.45 (s, 3, CH_3), 7.35-8.15 (m, 4, H-6.7,8.9), 8.5 (s, 1, H-10), 11.6 (s, 1, NH)
b	Ac	Ac	NAc_2	Ac_2O + Py	94.3	214-215	$C_{18}H_{17}N_5O_5$ 383.38	56.39 56.10	4.47 4.49	18.27 18.32	1740, 1720 (C=O)	2.25 (s, 3, CH_2), 2.45 (s, 3, CH_3), 2.5 (s, 6, CH_3), 7.5-8.15 (m, 4, H-6.7,8.9), 8.5 (s, 1, H-10)
c	Ac	CH_3	H	Ac_2O + Py	66	267-269	$C_{13}H_{12}N_4O_2$ 256.26	60.93 61.08	4.72 4.90	21.86 22.01	1700 (C=O)	2.25 (s, 3, CH_3), 3.27 (s, 3, CH_3), 7.4-8.0 (m,4, H-6.7,8.9), 8.3 (s, 1, H-10), 10.8 (s, 1, NH)
d	Ac	CH_3	CH_3	Ac_2O	94	156-157	$C_{14}H_{14}N_4O_2$ 270.27	62.21 62.37	5.22 5.37	20.73 20.68	1690 (C=O)	2.3 (s, 3, CH_3), 3.35 (s, 3, CH_3), 3.4 (s, 3, CH_3), 7.4-8.1 (m, 4, H-6.7,8.9), 8.35 (s, 1, H-10)

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