

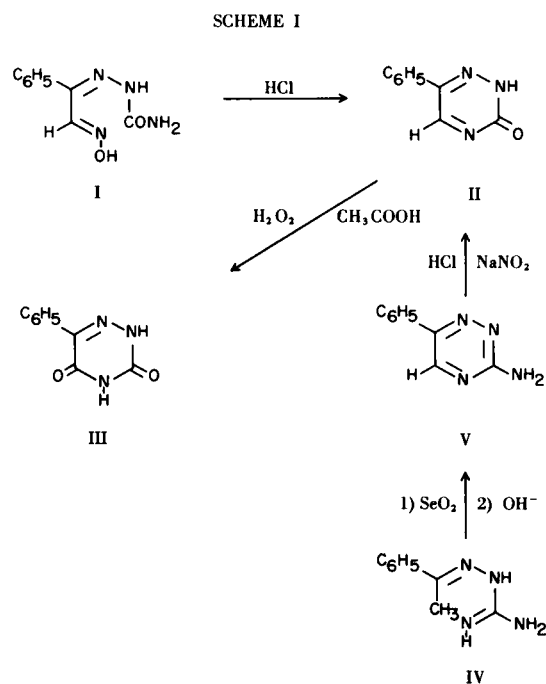
Acid Cyclization of Arylglyoxal Aldoxime Semicarbazone: Synthesis of 6-Aryl-*as*-triazine-3-(2*H*)-one

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In continuation of our study of the cyclization of substituted glyoxal aldoxime semicarbazones (2), we carried out the cyclization of phenylglyoxal aldoxime semicarbazone (I) (3) in acid medium. Compound I, refluxed in dilute hydrochloric acid gave an 83% yield of a white crystalline powder (II). The infrared spectrum of the compound obtained was found to be very similar to other *as*-triazines synthesized previously (2). Compound II on boiling with hydrogen peroxide in glacial acetic acid was converted to 6-phenyl-*as*-triazine-3,5-(2*H*,4*H*)-dione (III) in good yield.

Further confirmation of the structure of this new *as*-triazine (II) was obtained through an independent synthesis of II by selenium dioxide oxidation of acetophenone guanilhydrazone (IV), and its subsequent cyclization in aqueous potassium carbonate to 6-phenyl-3-amino-*as*-triazine (V). Oxidation of V with nitrous acid gave II in good yield (Scheme I).



New 6-aryl-*as*-triazine-3-(2*H*)-ones prepared by this method from the corresponding arylglyoxal aldoxime semicarbazones are tabulated in Table I.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage microscope and are uncorrected. The infrared spectra were determined with a Leitz Model III spectrograph, using potassium bromide discs. The N.M.R. spectra were determined with a Varian A-60A instrument.

3-Amino-6-phenyl-*as*-triazine (V).

Selenium dioxide, 1.33 g. (0.011 mole) was added to a solution of 1.76 g. (0.01 mole) of acetophenone guanilhydrazone (4) in 20 ml. of acetic acid and the mixture was stirred for one hour at room temperature. The reaction mixture was then boiled for 2 hours on a steam bath and the hot solution was filtered to remove the precipitated selenium. The filtrate was diluted with water and extracted a few times with chloroform. The extract was washed with water and the solvent was evaporated. The residue was refluxed for one hour with 20 ml. of 10% aqueous potassium carbonate. The reaction mixture upon cooling gave a yellow precipitate which was recrystallized from aqueous ethanol to give 1 g. (62%) of bright yellow needles, m.p. 198° (lit. (5) 197°); infrared spectrum, ν max cm^{-1} , 3450, 3250, 1670, 1640, 1595, 1520, 1485, 1450, 1370, 1125, 1040, 810, 755 and 675; NMR (DMSO), δ 7.3 (broad s, 2H, NH₂), 7.4-8.15 (m, 5H, C₆H₅), 8.8 (s, 1H, CH).
Anal. Calcd. for C₉H₈N₄: C, 62.77; H, 4.68. Found: C, 62.61; H, 4.81.

6-Phenyl-*as*-triazine-3-(2*H*)-one (II).

Method A.

To a cold solution of V, 1 g. (0.058 mole), in 20 ml. of 5% hydrochloric acid, was added with stirring a solution of 0.4 g. (0.058 mole) of sodium nitrite in 20 ml. of water. The reaction mixture was allowed to stand 3 hours at room temperature, and then was heated on a steam bath until the evolution of nitrogen ceased. The white precipitate obtained was recrystallized from acetic acid to give 0.6 g. of II (60%), m.p. 224-225°.

Method B.

A mixture of I (0.5 g.) and 15 ml. of 5% hydrochloric acid was refluxed for one hour during which time a white precipitate was formed. The compound was recrystallized as above to give 0.35 g. of II (83%), m.p. 225°. The infrared spectra of both compounds were identical; ν max cm^{-1} , 3200, 1690, 1425, 1312, 1264, 1160, 762 and 690.

TABLE I

6-Aryl-*as*-triazine-3-(2*H*)-ones

Aryl Group	Yield %	M.P. °C	Formula	Analysis	
				Calcd. %	Found %
<i>p</i> -CH ₃ C ₆ H ₄	92	207	C ₁₀ H ₉ N ₃ O	64.17 4.81	64.05 4.92
<i>p</i> -FC ₆ H ₄	82	217	C ₉ H ₆ FN ₃ O	56.54 3.14	56.31 3.06
<i>p</i> -ClC ₆ H ₄	84	203	C ₉ H ₆ ClN ₃ O	52.04 2.89	52.26 3.11
<i>p</i> -BrC ₆ H ₄	91	206	C ₉ H ₆ BrN ₃ O	42.85 2.38	42.79 2.31
<i>p</i> -CH ₃ OC ₆ H ₄	94	215	C ₁₀ H ₉ N ₃ O ₂	59.11 4.46	58.96 4.39
<i>p</i> -CH ₃ SC ₆ H ₄	80	203	C ₁₀ H ₉ N ₃ OS	54.79 4.11	54.51 4.32
<i>p</i> -NO ₂ C ₆ H ₄	82	228	C ₉ H ₆ N ₄ O ₃	49.59 2.77	49.52 2.71
β-C ₁₀ H ₇ (a)	75	208	C ₁₃ H ₉ N ₃ O	69.94 4.06	69.81 4.22

(a) β-Naphthylglyoxal aldoxime semicarbazone necessary for the synthesis of this compound, was prepared by the method described in Reference 2. The yield was 82%, m.p. 175°. *Anal.* Calcd. for C₁₃H₁₂N₄O₂: C, 60.93; H, 4.68. Found: C, 61.04; H, 4.52.

Anal. Calcd. for C₉H₇N₃O: C, 62.43; H, 4.07. Found: C, 62.16; H, 3.98.

6-Phenyl-*as*-triazine-3,5-(2*H*,4*H*)-diones (III).

A solution of 1 g. of II in 20 ml. of acetic acid and 10 ml. of 30% hydrogen peroxide was heated for 6 hours on a steam bath and then concentrated to a small volume under reduced pressure. The residue was diluted with hot water to precipitate unreacted starting material which was removed by filtration. The filtrate was evaporated and the residue was crystallized from dilute alcohol to give 0.60 g. (65%) of III, m.p. 262°. This compound was identical with the compound prepared by alkaline cyclization of I (2).

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