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SYNTHESIS AND PROPERTIES OF BIS-/1,3,5-TRIMETHYL-2,4-DIOXOHEXAHYDRO-1,3,5-TRIAZINYLIDENE-(6)/

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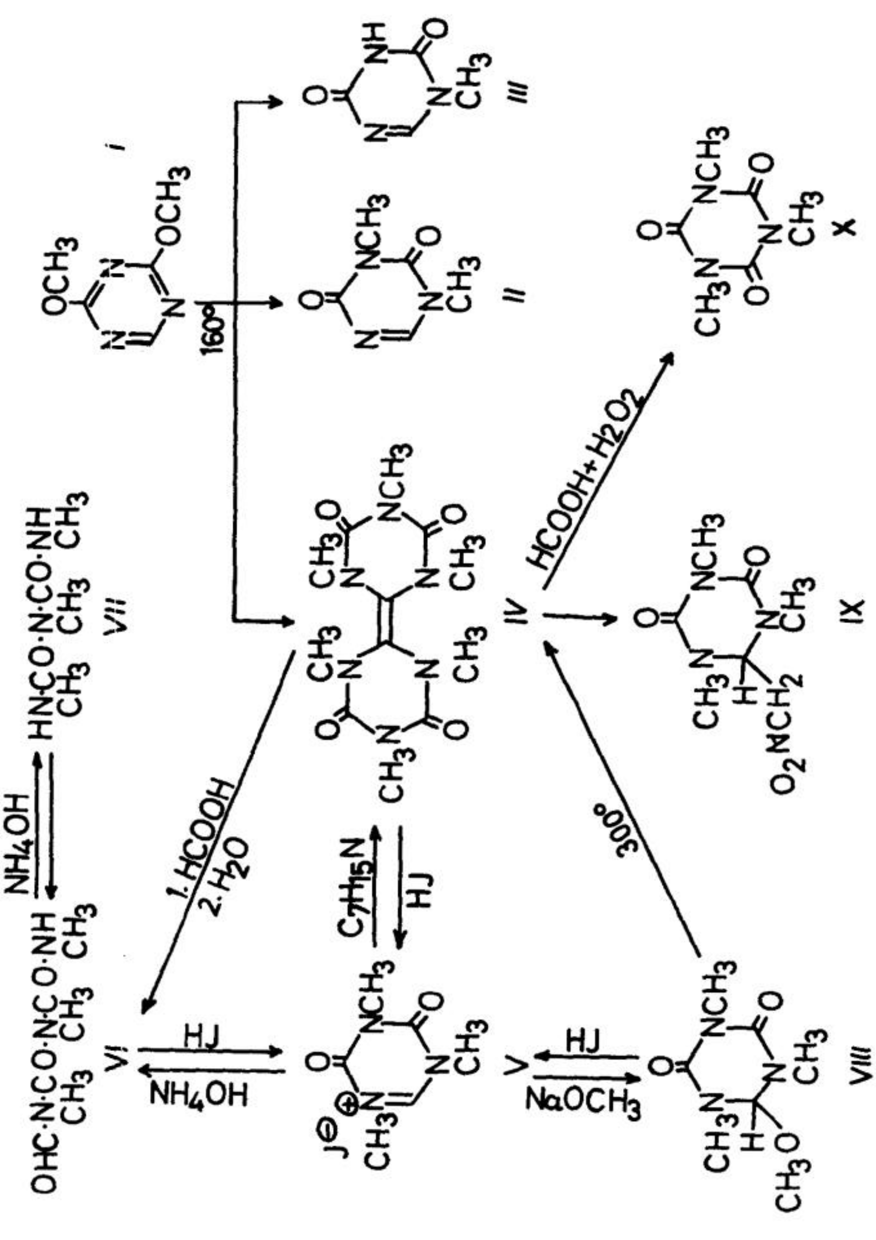
As is well known, heating of methoxytriazines to higher temperatures results in a shift of the methyl groups to nitrogen (1,2).

In attempting to rearrange thermally the methyl groups of 2,4-dimethoxy-1,3,5-triazine (I) we were able to isolate after 10 h at 160°C 26% of the expected dimethyltriazine II (m.p. 164°C without depression on mixing with an authentic sample) plus a surprising amount of 35% of the monomethyl derivative III (m.p. 212-214°C without depression with an authentic sample) as well as 23% of a new compound to which the structure of bis-/1,3,5-trimethyl-2,4-dioxohexahydro-1,3,5-triazinylidene-(6)/ IV is attributed. No such compounds have been prepared in the triazine series so far. Recently similar compounds were described in the imidazole group by Wanzlick (3).

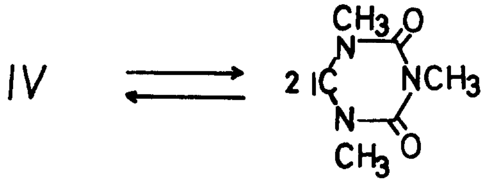
Bis-triazinylidene IV does not melt in a sealed capillary below 350° but sublimes substantially above 310°C with partial decomposition. Its solubility is very poor in all


I
II
III
IV
V
VI
VII
VIII
IX
X
160°
300°
NH₄OH
1. HCOOH
2. H₂O
C₇H₁₅N
HJ
NaOCH₃
HCOOH+H₂O₂
OHC·N·CO·N·CO·NH
HN·CO·N·CO·N·CO·NH

solvents tested. It can be recrystallized from dimethylformamide, however.

Mass spectrometry permitted to determine its molecular weight as 310 ($C_{12}H_{18}N_6O_4$, calcd. 310). Particles of half molecular weight have not been found. In the UV spectrum ($\lambda_{max}^{H_2O}$ 244 mμ, logε 4.40) bis-triazinylidene IV has a maximum at the same wavelength as dimethyltriazine II ($\lambda_{max}^{H_2O}$ 244 mμ, logε 3.70) but shows a much greater hyperchromic effect. In the carbonyl region of the IR spectrum ($\nu_{max}^{dioxane}$ 1696 cm^{-1} and 1731 cm^{-1}) the compound has two maxima corresponding to carbonyl groups but in comparison with other dioxotriazines it has no absorption band near 1620 cm^{-1} which is characteristic for the C=N bond of these compounds. The symmetrically substituted double bond of bis-triazinylidene IV is not apparent in the IR spectrum in agreement with theoretical expectation.

According to Wanzlick´s (3) views developed for elucidating some reactions of substances of this type in the imidazole group one could expect in this case a cleavage of bis-triazinylidene IV to nucleophilic carbene IVa, the formation of this reactive monomer explaining some chemical reactions of this compound.



(IVa)

Brief heating of bis-triazinylidene IV with concentrated hydroiodic acid 36% methoiodide V was obtained (m.p. 204-206°C, decomposing) which was identical with the product formed by the action of methyliodide in a sealed tube at 100°C on dimethyltriazine II. Methoiodide V yields on standing in water-free pyridine with excess N-ethylpiperidine the bis-triazinylidene IV (53%). In this reaction one must assume the formation of intermediate carbene IVa which spontaneously dimerizes to IV in an aprotic medium. Aqueous solution of V reacted with excess silver carbonate or ammonia to 57% formyltrimethylbiuret VI (m.p. 139-140°C) which was further heated with ammonia to 100°C to hydrolyse to the well-known 1,3,5-trimethylbiuret (VII) (75%, m.p. 125-126°C without depression with an authentic sample). Treatment with hydrogen iodide at room temperature for 30 min converted VI to 84% V (m.p. 204-206°C, decomposing). Formylbiuret VI was also obtained directly from IV by a brief heating with 100% formic acid and several-fold evaporation with water (70%). Finally VI could be also obtained by formylating biuret VII with the Vilsmeier complex (81%). Reaction of an equimolar amount of sodium methoxide with methoiodide V in absolute methanol, evaporation and extraction of the residue with benzene led to 56% methoxytriazine VIII (m.p. 61-63°C) which yielded 38% bis-triazinylidene IV on short heating to 300°C. Brief treatment with hydrogen iodide at room temperature converted VIII to 80% V (m.p. 204-206°C, decomposing). Heating of IV in a sealed tube with nitromethane to 150°C for 12 h resulted in 35% nitromethyltriazine IX (m.p. 158-160°C) and oxidation with performic acid (1 h at 100°C) yielded 46% trimethylisocyanurate (X) (m.p. 176-178°C without depression with an authentic sample).

The above reactions of bis-triazinylidene IV are similar to reactions of analogous compounds of the imidazole series but proceed much more slowly. At the same time, they appear to confirm the proposed structure IV.

Satisfactory analytical data were obtained for all compounds cited.

A detailed account of the work carried out will be shortly published in the Collection of Czechoslovak Chemical Communications.

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