1,2,3,5-Tetrazinones and Zwitterionic 1,2,4-Triazolin-3-ones

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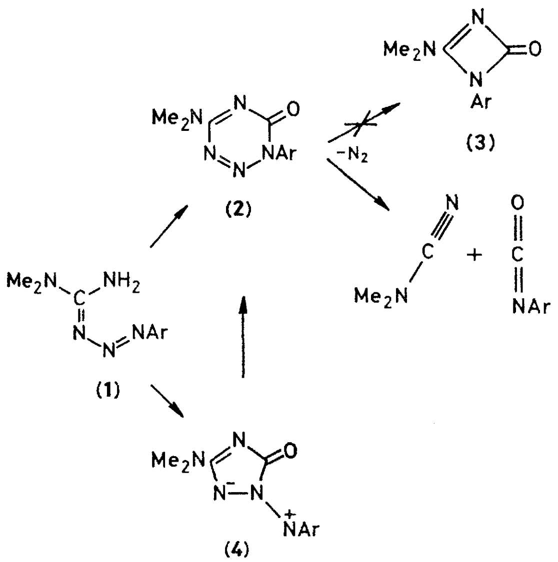
Treatment of 2-arylazo-1,1-dimethylguanidines (**1**) with phosgene yields the novel 1,2,3,5-tetrazinones (**2**), together with isomeric dipolar triazolinones (**4**); both types of product decompose to give nitrogen, dimethylcyanamide, and aryl isocyanate.

1,2,3,5-Tetrazines have been elusive[1] but for the formation of some complex cyanoamino-derivatives in the electrolytic oxidation of cyanamide.[2] We were interested in the 1,2,3,5-tetrazine system as a potential precursor of 1,3-diazetes and now report on the synthesis of 1-aryl-4-dimethylamino-1,2,3,5-tetrazin-6-ones (**2**).

The triazenes (**1a**—**c**),† obtained in 74, 81, and 42% yields, respectively, by coupling of 1,1-dimethylguanidine with the appropriate arenediazonium fluoroborate, reacted with phosgene in the presence of pyridine to give up to 43% of the tetrazinones (**2a**—**c**),† cream to pale-yellow solids, which melted with decomposition in the range 115—125 °C. Their i.r. spectra, which exhibited strong carbonyl bands at 1700—1712 cm^{-1}, ^{1}H n.m.r. spectra, which showed only the presence of dimethylamino- and aryl-substituents, and u.v. absorptions (in EtOH) at 315, 325, and 340 nm, respectively, are in accordance with the proposed structures. Final confirmation was obtained by an *X*-ray analysis‡ of compound (**2a**). The mass spectra of the tetrazinones contained peaks corresponding to aryl isocyanate (100%) and dimethylcyanamide (30—35%); thermal decomposition in boiling toluene likewise gave these fragments, but there was no evidence for the formation of the diazetinones (**3**).



Scheme 1. **a**; Ar = Ph
b; Ar = p-MeC$_6$H$_4$
c; Ar = p-MeOC$_6$H$_4$

The i.r. spectra of the crude products of the phosgene reactions contained bands near 1800 cm^{-1} and two compounds showing these absorptions were isolated by column chromatography. The p-tolyltetrazinone (**2b**) was accompanied by a deep-yellow isomer (4%),† m.p. 183 °C (decomp.), ν_{max} 1800, 1640, and 1500 cm^{-1}, and λ_{max} (EtOH) 225 and 402 nm. Its structure was solved by *X*-ray analysis,‡ which showed it to be the betaine (**4b**). The p-methoxyphenyl-analogue (**4c**)† was obtained as orange needles (8%), m.p. 190 °C (decomp.), i.r. 1790, 1640, and 1500 cm^{-1}, λ_{max} 266 and 425 nm.

The betaines (**4b**, **c**) decomposed in boiling o-dichlorobenzene to yield the corresponding aryl cyanates and dimethylcyanamide; their mass spectra were almost identical with those of the isomeric tetrazinones. This suggests (see Scheme 1) that the triazolinones rearrange to the tetrazinones, which then fragment.

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References

1 For an account of attempts to prepare 1,2,3,5-tetrazines, see J. G. Erickson, in 'The 1,2,3- and 1,2,4-Triazines, Tetrazines, and Pentazines,' 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York, 1956, p. 177; see also P. F. Wiley, in 'Chemistry of 1,2,3-Triazines and 1,2,4-Triazines, Tetrazines, and Pentazines,' 'The Chemistry of Heterocyclic Compounds,' eds. A. Weissberger and E. C. Taylor, Wiley, New York, 1978, p. 1296.

2 K. Kubo, T. Nonaka, and K. Odo, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1339.

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† Satisfactory analytical data were obtained.

‡ Details of the *X*-ray analysis will be published elsewhere.