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A NOVEL s-TETRAZINE ASSEMBLY

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There have been no reports, either in reviews on sym-tetrazines [1-3] or in periodicals, of the synthesis of sym-tetrazines which are bonded directly to one another by C–C bonds. The preparation of the azo-compound (Ia) has been reported [4], but it was not possible to recrystallize this compound as a result of its low solubility.

We have found that on heating a suspension of (Ia) in DMF or o-dichlorobenzene to above 90°C, nitrogen is evolved rapidly with the formation of 77% of 6,6'-diphenyl-3,3'-bis-s-tetrazine (II) as a reddish-brown solid (λ_{max} 487 nm), mp 301-308°C (from DMF). M^+ 314.

IIa, b Ia, b

I, II a $R=C_6H_5$; b $R=4-ClC_6H_4$

Alternative structures for (IIa) in which the sym-tetrazine ring is external with respect to R, which could arise by other modes of recombination of the phenyl-s-tetrazinyl radicals formed by elimination of nitrogen, are excluded by comparing the PMR spectra of (IIa) and the model 3-phenyl-s-tetrazine. In the latter, the tetrazine ring proton resonates at δ 10.6 ppm, whereas in (IIa) only a broadened multiplet centered on δ 7.7 ppm is seen for the phenyl protons. In addition, (Ib), obtained by the general method of Ershov and Postovskii [4], in which the p-positions of the benzene rings are occupied by chlorine atoms, also loses molecular nitrogen to give 75% of the bis-s-tetrazine (IIb) as a reddish-brown solid, mp 310-312°C, M^+ 382.

Unlike mono-s-tetrazines, which undergo cycloaddition with elimination of nitrogen [5], the bis-s-tetrazines (II) add to unsaturated compounds (enamines, acenaphthylene, tolane, ketones in the presence of triethylamine, and exomethylene anhydro-bases) without loss of nitrogen.

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