

## Reactions of Arylaldehyde Azines with Strong Bases and the Mechanism of Formation of 1,2,4-Triazoles

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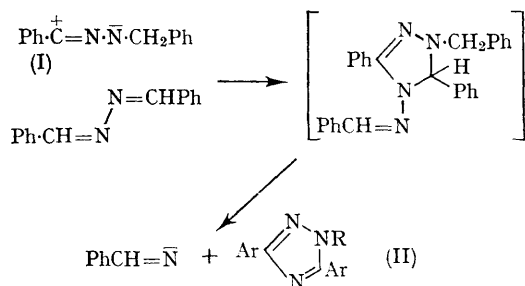
ARYLALDEHYDE HYDRAZONES, structurally unsuitable for Wolff-Kishner reductions (*N*-substituted hydrazones, azines, hydrazidines, *etc.*) have been shown recently to yield acyclic and heterocyclic products on treatment with strong bases.<sup>1,2</sup> We now report a study of arylaldehyde azines which helps to clarify the mechanisms of these reactions.

Treatment of benzaldehyde azine with potassium *t*-butoxide (1–2 moles) in boiling toluene for 40 hr. resulted in complete reaction, and eleven products have been isolated. Major components were 3,5-diphenyl-1,2,4-triazole (III; Ar = Ph) and its 1-benzyl derivative (II; Ar = Ph, R = CH<sub>2</sub>Ph), 3,5,6-triphenyl-1,2,4-triazine and two of its reduction products, 2,4,5-triphenylimidazole and benzoic acid. Traces of *trans*-stilbene, 3,4,5-triphenylpyrazole, and 2,4,6-triphenyl-1,3,5-triazine were formed also, and in

some experiments benzonitrile was isolated in small yield.

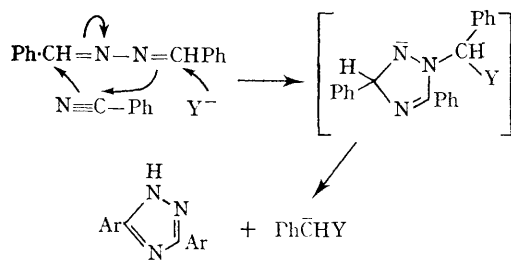
The structure of the benzyltriazole (II; Ar = Ph, R = CH<sub>2</sub>Ph) suggests that it is formed by 1,3-addition of benzaldehyde azine or its tautomer to benzonitrile or to a species containing a C=N group. Consistent with this postulate is the isolation of the 1-(diphenylmethyl)triazole (II; Ar = *m*-MeO·C<sub>6</sub>H<sub>4</sub>, R = CHPh<sub>2</sub>) and *m*-methoxybenzonitrile from reaction of the unsymmetrical azine, *m*-MeO·C<sub>6</sub>H<sub>4</sub>CH=N-N=CPh<sub>2</sub>, with potassium *t*-butoxide.

Repetition of the benzaldehyde azine reaction in the presence of labelled benzonitrile, Ph<sup>14</sup>CN, afforded the diphenyltriazole (III; Ar = Ph) containing over 30% of the original radioactivity, but labelling in other heterocyclic products was negligible. It is clear, therefore, that the 1-benzyltriazole does not arise from benzonitrile



and we suggest the following mechanism in which the dipolar species (I, only one mesomeric form shown) undergoes 1,3-cycloaddition with a second molecule of benzaldehyde azine. The reactions of diphenylnitrile imine<sup>3</sup> provide an analogy for this scheme.

One route to 3,5-diphenyl-1,2,4-triazole (III; Ar = Ph) must proceed by base-catalysed loss of the side-chain from the 1-benzyltriazole, since we find that this occurs under the conditions of the azine-butoxide reaction. The tracer experiment, however, indicates that a second pathway involves benzonitrile, and the following mechanism is possible.



The nucleophile,  $\text{Y}^-$ , may be the anions  $\text{PhCH}=\text{N}^-$  (from elimination of benzonitrile from benzaldehyde azine) or  $\text{Ph}\bar{\text{C}}=\text{N}-\text{N}=\text{CHPh}$ , which would provide good leaving groups for subsequent elimination, or less likely the *t*-butoxide ion.

Spassov and Robev<sup>2</sup> reported the formation of diaryl-1,2,4-triazoles from arylaldehyde azines and sodamide in xylene, and suggested that one nitrogen atom of the product was derived from the amide anion. We consider it more likely that sodamide acts only as a base, and that the triazoles are formed by mechanisms similar to those suggested above.

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<sup>1</sup> R. F. Smith and L. E. Walker, *J. Org. Chem.*, 1962, **27**, 4372; S. Robev, *Compt. rend. Acad. bulg. Sci.*, 1959, **12**, 141, 207; M. F. Grundon and M. D. Scott, *J. Chem. Soc.*, 1964, 5674.

<sup>2</sup> A. Spassov and S. Robev, *Chem. Ber.*, 1965, **98**, 928.

<sup>3</sup> R. Huisgen, R. Grashey, E. Aufderhaar, and R. Kunz, *Chem. Ber.*, 1965, **98**, 642.