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New Synthesis of 1,2,3-Triazoles

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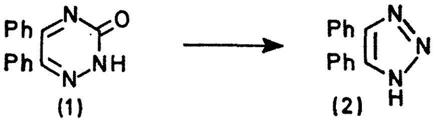
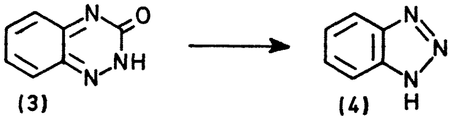
Summary Treatment of 1,2,4-triazin-3(2*H*)-ones with ethereal chloramine at room temperatures gives 1,2,3-triazoles in high yield.

ATTEMPTED amination of 1,2,4-triazin-3(2*H*)-ones with hydroxylamine-*O*-sulphonic acid gave imidazolin-2-ones by loss of nitrogen from the unstable *N*-amino-derivatives.[1] Attempted amination with ethereal chloramine at room temperature led to another, equally unexpected, ring contraction to 1,2,3-triazoles, with formal extrusion of carbon monoxide. Thus 5,6-diphenyl-1,2,4-triazin-3(2*H*)-one (**1**) gave 4,5-diphenyltriazole (**2**) (94%), benzo-1,2,4-triazin-3(2*H*)-one (**3**) gave benzotriazole (**4**) (65%), and the dibenzo-derivative of (**3**) gave 9,10-phenanthrotriazole (92%). No *N*-amino-compounds or their decomposition products were detected. In each case ammonium chloride separated from the ethereal solution almost quantitatively. Chloramine thus acts as an oxidant, probably by initial conversion of the triazinones into their *N*-chloro-derivatives. This is supported by the similar conversion of diphenyltriazinone (**1**) into diphenyltriazole (**2**) by aqueous sodium hypochlorite and acetic acid (52%) and by *N*-chlorobenzotriazole in benzene (100%). *N*-Chlorination could be followed by a Favorskii type rearrangement (Scheme) or by a ring opening and closing sequence to give an *N*-substituted triazole which is hydrolysed to the parent triazole isolated.



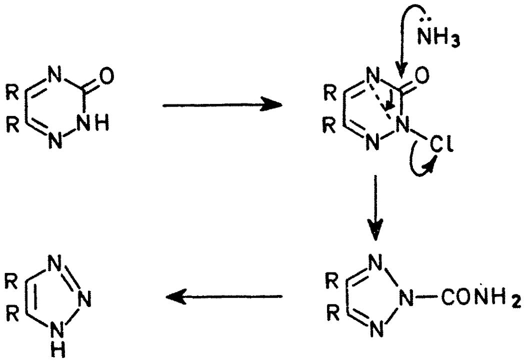
(**1**) (**2**)



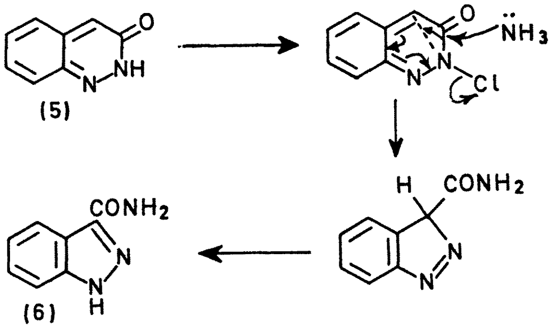
(**3**) (**4**)

This oxidation provides a new simple route to 1,2,3-triazoles, particularly useful for 4,5-diaryltriazoles which are not otherwise readily accessible; the required triazinones are easily made from benzils and semicarbazide.[2]

In a variation of this oxidative ring contraction, treatment of benzotriazinone (**3**) with lead tetra-acetate in boiling benzene gave 1-acetylbenzotriazole (90%), presumably by the same general mechanism.



SCHEME



(**5**) (**6**)

Reaction of the analogous cinnolin-3(2*H*)-one (**5**) with chloramine was more complex; the two major products were 4-chlorocinnolin-3(2*H*)-one (20%), the product of *C*-chlorination, and indazole-3-carboxamide (**6**) (20%), again possibly the product of *N*-chlorination followed by ring contraction as shown.

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[1] C. W. Rees and A. A. Sale, preceding communication.

[2] J. P. Horwitz in "Heterocyclic Compounds", ed. R. C. Elderfield, vol. 7, p. 759, Wiley, New York, 1961.