# Synthesis of 1,2,3-Triazoles by Reaction of Azide Ion with αβ-Unsaturated Nitro-compounds and Nitriles

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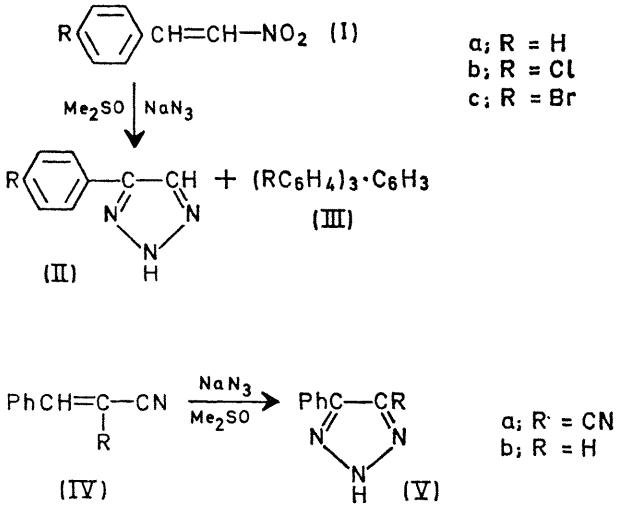
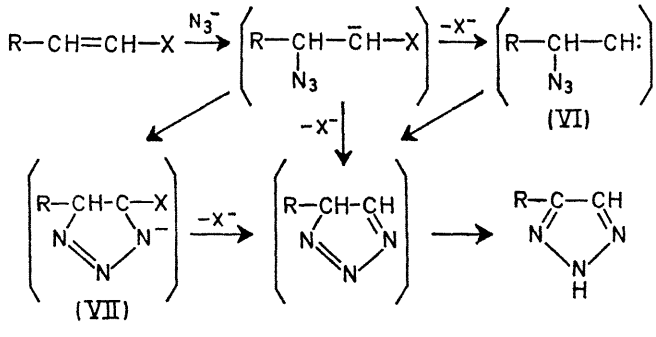
*Summary* The synthesis of 1,2,3-triazoles by reaction of αβ-unsaturated nitro-compounds and nitriles with sodium azide is described.

WE have investigated the reactions of sodium azide with αβ-unsaturated nitro-compounds and nitriles and found that




with a series of *trans*-arylnitroethylenes (Ia—c) in dimethyl sulphoxide or dimethylformamide at room temperature the respective triazoles (IIa—c) (60%) were obtained. Unexpectedly the reaction also gave considerable quantities of *sym*-triarylbenzenes (IIIa—c). In another experiment it was shown that phenylacetylene does not trimerize under these conditions; thus it cannot be an intermediate.

The dinitrile (IVa) gave the triazole (Va)(40%) with sodium azide in $Me_2SO$ at 20°. *trans*-Cinnamonitrile (IVb) at 70° gave a complex mixture from which (Vb) (10%) and, unexpectedly, (Va) (10%) were isolated.




The formation of the foremention by-products indicates a complicated mechanism, which can be formally discussed in terms of nucleophilic substitution by the azide ion at the olefinic carbon atom. Thus direct displacement of $NO_2$ or CN by $N_3$ and cyclization of the vinylazide fragments is possible. Although few examples of triazole synthesis have

been described which can be assumed to occur *via* substituted vinylazide intermediates,[1-4] simple vinylazides do not undergo cyclization to triazoles.[5] It should be noted that α- and β-styrylazides are not intermediates since they are thermally unstable and even under these mild conditions rearrange to azirine derivatives.[6,7] It is most probable that the azide anion attacks the double bond, and that azidocarbene (VI) or triazoline (VII) are possible intermediates.

However, in all the reactions studied triazoles are the major products. Thus, the reaction of αβ-unsaturated nitriles and nitro-compounds with sodium azide may be regarded as a novel synthesis of triazoles.

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