NOVEL HETEROCYCLES BY REACTION OF NITROALKENES AND YNAMINES D.N. Reinhoudt, W.P. Trompenaars and A.D. de Wit

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In the course of our work on (2+2)-cycloadditions of substituted heteroaromatic compounds with acetylenes reactions of nitroalkenes and nitroheteroaromatics with ynamines have been investigated.

We found that nitroalkenes react with ynamines at room temperature to give three different types of 1:1 reaction products \underline{viz} . 3-nitrocyclobutenes ($\underline{1}$), nitrones ($\underline{2}$) and 2,3-dihydro-azet-N-oxides ($\underline{3}$). The latter type of product represents the first well-established examples of "stable" 4-membered cyclic nitrones. Their structure has been unequivocally established by single-crystal X-ray analysis. These cyclic nitrones yielded the expected bicyclic 1,3-dipolar adducts ($\underline{4}$) with DMAD. From the reactions of ynamines with 3-nitro-1-benzothiophen and with 4-nitroisothiazole mixtures of nitrone ($\underline{2}$) and cyclobutenes ($\underline{1}$) were obtained. The corresponding cyclic nitrones were absent in these reaction mixtures.

3-Nitro-1-benzofuran reacts with ynamines in a completely different manner. Three 1:1 reaction products were obtained viz. a 1-benzoxepin $(\underline{5})$, a quinoline N-oxide $(\underline{6})$ and a 1,2-benzisoxazole N-oxide (7).

Formation of 2,3 and 5-7 in these reactions proceeds via a 1,4-dipolar intermediate.

1. D.N. Reinhoudt, Adv. Heterocycl. Chem. 21, 253 (1977).