

Robertus P. M. Berbee and Clarisse L. Habraken*

Gorlaeus Laboratory, The University, Leiden, The Netherlands

Received October 21, 1980

Preparation of the C-N coupled tripyrazolyl VII, by two consecutive cine substitution reactions starting from 1,4-dinitropyrazole and using pyrazole as a nucleophile, is described. Solvent dependent nitrations of 4-nitro-3(5)-(1'-pyrazolyl)pyrazole I are reported.

J. Heterocyclic Chem., **18**, 559 (1981).

Recently we reported on the cine substitution reaction of 1,4-dinitropyrazoles (1,2). In this reaction, a nucleophilic aromatic substitution of the 1,2-addition elimination type, the entering group comes in *ortho* to the leaving group resulting in the formation of a 3*H*-pyrazole. The ultimate product is then formed in a subsequent fast 1,5-hydrogen shift. In the case of pyrazoles as nucleophiles (1) this cine substitution reaction affords bipyrazolyls. In

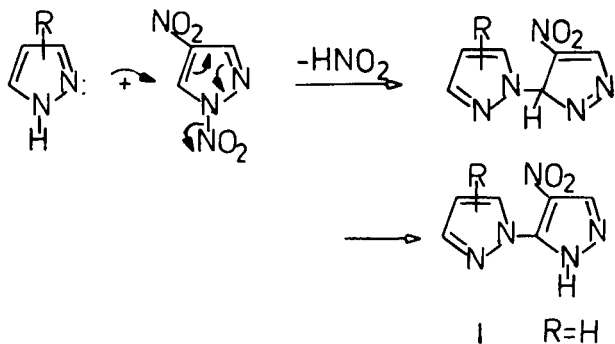
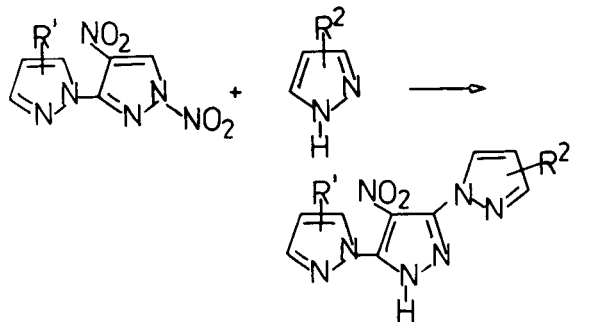


Chart 1

view of the excellent yields generally obtained in this reaction we expected that *N*-nitration of 4-nitro-3(5)-(1'-pyrazolyl)pyrazole I followed by a second cine substitution reaction with a pyrazole would provide a convenient method for the synthesis of twice C-N coupled tripyrazolyls of the general structure II. The feasibility of



III $R^1 = H$
IV $R^1 = 4\text{-NO}_2$
II $R^1 = R^2 = H, \text{alkyl, aryl}$
VII $R^1 = 4\text{-NO}_2, R^2 = H$

Chart 2

performing this cine substitution reaction on a 1,4-dinitropyrazole containing a large bulky group in the 3-position was demonstrated recently by J. Grant Buchanan, *et al.*, in their elegant new synthesis of formycin (3).

Nitration of I in acetic acid with nitric acid followed by addition of acetic anhydride according to the procedure described previously (4) was unsuccessful. Only starting material I was recovered from the reaction mixture. However, treatment with acetyl nitrate, *i.e.*, a freshly prepared mixture of nitric acid and acetic anhydride, gave instead of the wanted dinitro bipyrazolyl III the trinitro derivative IV contaminated with the *N*-acetyldinitro bipyrazolyl V. The structure assignments of IV and V were

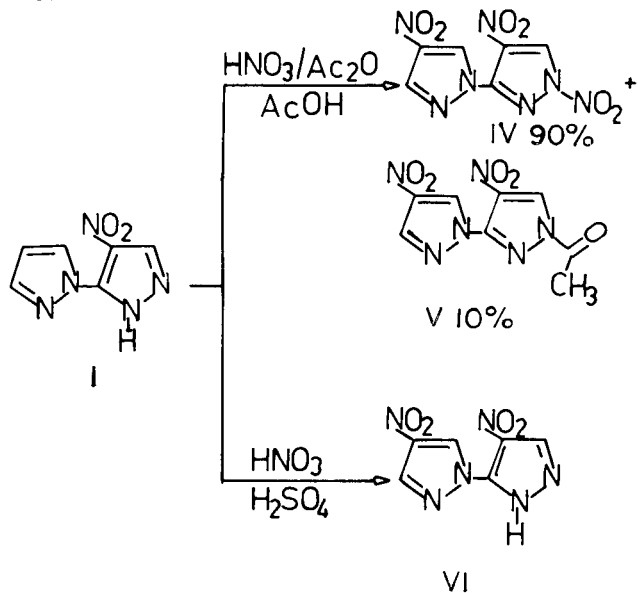


Chart 3

primarily based on their proton nmr data. Acid hydrolysis of a sample of this reaction product followed by recrystallization gave 4-nitro-3(5)-(4'-nitro-1'-pyrazolyl)pyrazole VI. This dinitro bipyrazolyl VI was shown to be identical with an authentic sample obtained from the nitration of I with nitric acid in sulfuric acid.

The crude compound IV reacted readily with pyrazole at room temperature in acetonitrile solution. From the

