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1-Hydrazonyltetrazoles: Fragmentative Cyclisation - A New Route to Substituted 1,2,4-Triazoles.

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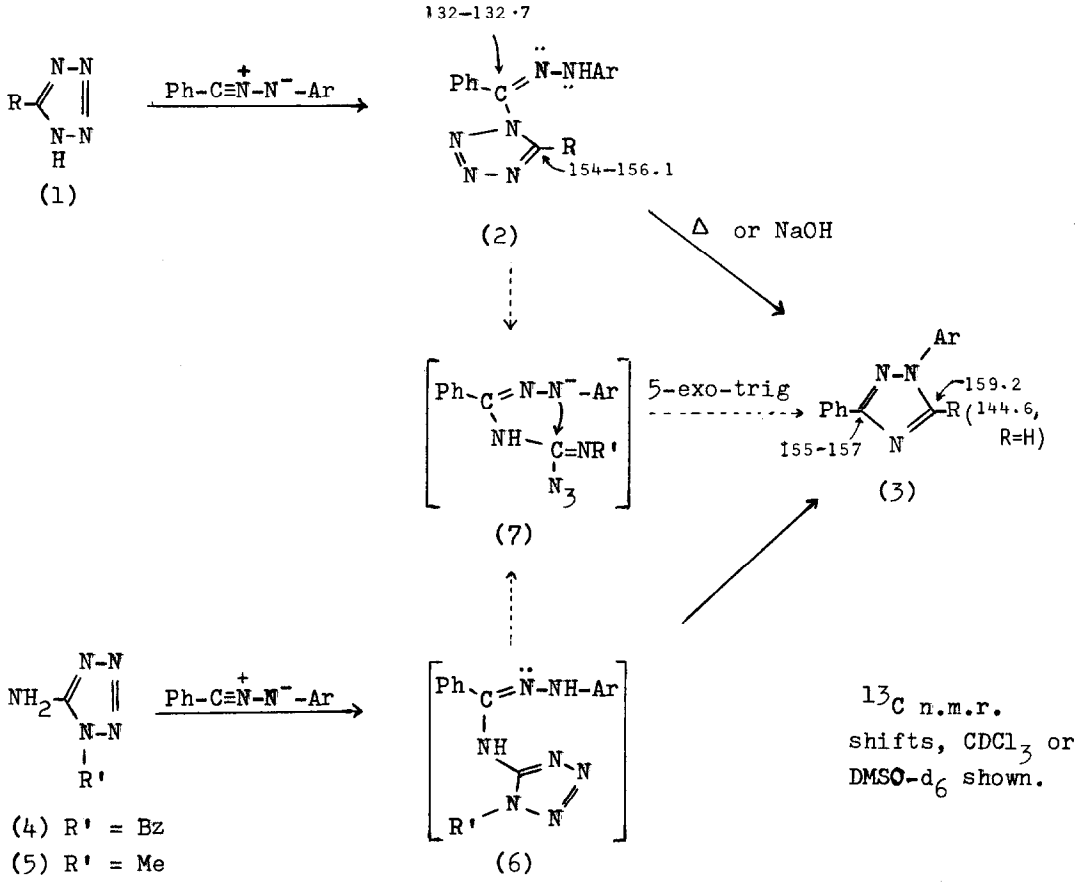
Summary: The reaction of tetrazole and some 5-aminotetrazoles with C-phenyl-N-4-nitrophenyl-nitrileimine gave 1-hydrazonyltetrazoles which fragmented and cyclised to 1,2,4-triazoles with overall loss of HN_3.

Electrophilic attack on tetrazoles which usually occurs preferentially at the 2-N-position, has been studied for a range of electrophiles but the reaction with nitrileimines has not been reported.[1-3] A recent report[4] of the reactions of nitrile oxides with some 5-alkyl- and -aryltetrazoles prompts us to make a preliminary report of interesting reactions of some 5-aminotetrazoles with C-phenyl-N-4-nitrophenyl nitrileimine which provides a new route to substituted 1,2,4-triazoles.

When compounds (1a) and (1b) were treated† with the nitrileimine in ethanol at 0-5°C the first 1-hydrazonyltetrazoles (2a) (m.p. 283-4°C) and (2b) (m.p. 146-147°) were isolated in 70% and 65% yields respectively (Scheme). These compounds were characterised by ^{1}H and ^{13}C n.m.r. spectra which showed them to be 1,5-disubstituted tetrazoles (5-C shift, 154-156 ppm).[5] On being heated under reflux in ethanol for 3h. or in ethanolic NaOH for 10 min. the molecules fragmented and cyclised to the triazoles (3a) (m.p. 283-4°; 84%) and (3b) (m.p. 160-161°; 90%) (Scheme). Treatment of tetrazole (1c) with the nitrileimine gave the triazole (3c) (m.p. 199-201°; 70%) directly and the intermediate (2c) could not be isolated even at -20°C. The structure of compound (3a) was confirmed unequivocally by its formation from the addition of cyanamide to the nitrileimine. Compound (3b) was also obtained by benzylation of (3a) with benzyl chloride and base.

Interstingly the product (3b) was again obtained in high yield when 1-benzyl-5-aminotetrazole (4) was treated with the nitrileimine in boiling ethanol. A similar reaction with compound (5) gave the product (3f) (m.p., 188-190°C,70%). Intermediates of type (2) cannot be involved in this reaction [compound (4) did not rearrange to (1b) under the conditions] and the NH_2 group probably added to the nitrileimine initially when the ring NH was blocked. An intermediate could not be isolated from this reaction but trace quantities of an unstable species which changed to (3b) on being dissolved in normal n.m.r. solvents and which showed i.r. absorption at ν_{max} 2116 cm^{-1} were encountered possibly indicating an azido or carbodiimide intermediate.

Treatment of the tetrazoles (1d) and (1e) with the nitrileimine gave the products (2d) (m.p. 215-217; 30%) and (2e) (m.p. 218-220°; 50%) (along with traces of 2-N-isomers and hydrazonyl ether from solvent addition). Compounds (2d) and (2e) were stable and did not



Scheme R = (a) NH_2; (b) NHBz; (c) H; (d) Me; (e) Ph; (f) NHMe

fragment on being heated in solution or treated with base. A common intermediate (7) could be involved in the reactions with the aminotetrazoles.

References and Notes.

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† General Procedure: A mixture of N-4-nitrophenylbenzhydrazonyl bromide (1m.mole) and the substituted tetrazole (1m.mole) in ethanol (10 ml.) was stirred at 0-5°C and treated dropwise with a solution of triethylamine (1m.mole) in ethanol (5 ml.). The products (2) separated after 1-2h.stirring. If the reaction is carried out under reflux the products (3) separate on cooling or they may be obtained by separate heating of the products (2).

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