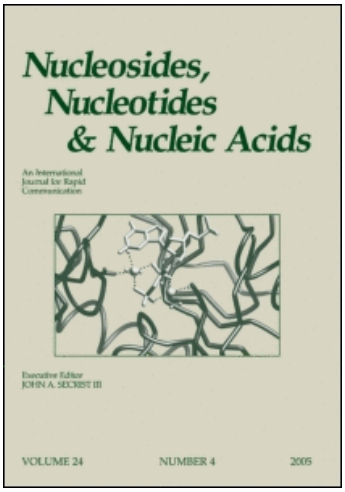


Nucleosides, Nucleotides and Nucleic Acids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597286

Reactions of 5-β-D-Ribofuranosyl Tetrazoles with Dipolarophiles

M. Prhavc[a]; L. B. Townsend[b]; J. Kobe[a]
[a] Boris Kidrič Institute of Chemistry, Ljubljana and Krka, Chemical and Pharmaceutical Works, Novo mesto, Yugoslavia [b] Department of Medicinal Cemistry, College of Pharmacy and Department of Chemistry, University of Michigan, Ann Arbor, MI, U.S.A.

To cite this Article Prhavc, M. , Townsend, L. B. and Kobe, J.(1991) 'Reactions of 5-β-D-Ribofuranosyl Tetrazoles with Dipolarophiles', Nucleosides, Nucleotides and Nucleic Acids, 10: 1, 729 — 730
To link to this Article: DOI: 10.1080/07328319108046584
URL: http://dx.doi.org/10.1080/07328319108046584

NUCLEOSIDES & NUCLEOTIDES, 10(1-3), 729-730 (1991)

REACTIONS OF 5-β-D-RIBOFURANOSYL TETRAZOLES WITH DIPOLAROPHILES

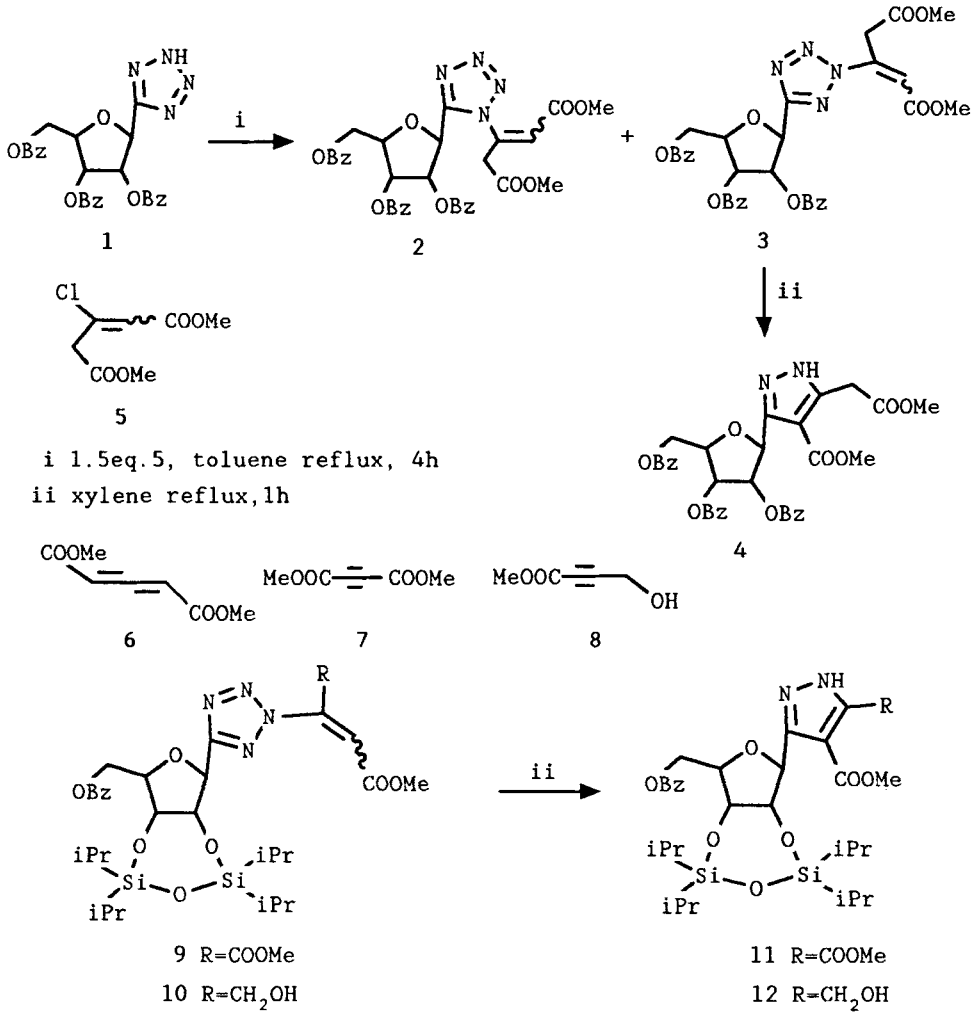
[a]M. Prhavc, [b]L. B. Townsend and [a]J. Kobe*

[a]Boris Kidrič Institute of Chemistry, Ljubljana and Krka, Chemical and Pharmaceutical Works, Novo mesto,Yugoslavia; [b]Department of Medicinal Cemistry, College of Pharmacy and Department of Chemistry, University of Michigan, Ann Arbor, MI, U.S.A.

Abstract: A two step transformation of protected 5-β-D-ribofuranosyl tetrazoles into pyrazole derivatives is described.

The synthesis of 5-ribosyl pyrazoles *via* nitrilimines generated *in situ* did not give satisfying results[1]. Therefore, a two step cycloaddition was thought for, using milder conditions to perform first the alkylation on the tetrazole[2] The alkenyl intermediate was then thermally rearranged into the anticipated pyrazole. Reactions[3] of protected tetrazoles (**1**) with dipolarophiles **5** - **8** gave N-1 and N-2 alkenyl substituted tetrazoles as major products[4]. Regioselective addition of allene **6** afforded N-2 isomer **3**, whereas the acrylate **5** furnished a mixture of isomers **2** and **3** in an 1:4 ratio. Acetylenes **7** and **8** also yielded mixtures of N-1 and N-2 isomers (1:1). Only N-2 alkenyl isomers **3**, **9** and **10** were thermally rearranged in xylene into pyrazoles **4**[5], **11** and **12**, respectively, *via* ring opening by loss of nitrogen and subsequent intramolecular cyclization of the 1,5-dipole; only one of the two possible positional isomers (**4**, **11**, **12**) was isolated. Besides, 2',3',5'-tri-O-benzoyl-β-D-ribofuranosylnitrile was formed upon the reaction of **3** into **4**, probably originating from a *zwitterionic* intermediate.

The structures of products were confirmed on the basis of ^{1}H, ^{13}C and ^{15}N-NMR techniques.



REFERENCES

1) Kobe, J.; Prhavc, M; Hohnjec, M.; Townsend, L. B. *Nucleosides & Nucleotides*, **1987**, *6*,365.
2) Woerner, F.; Reimlinger, H. *Chem. Ber.*, **1970**, *103*, 1908.
3) Reaction conditions **i** with dipolarophiles others than **5**: 1.1eq.**6**, toluene 0°C, 1day; 1.1eq.**7**, xylene reflux,5min.; 3.3eq.**8** added in portions over 3 days,toluene,r.t.
4) Total yields of both isomers after purification by flash chromatography were up to 60%.
5) mp 150-152°C(from EtOH); after debenzoylation with NaOMe/ MeOH : ms m/z = 330.1060($M^+[C_{13}H_{18}N_2O_8]$= 330.106304).