P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2012,(6), (1) :41-44

Synthesis of 6-Aziridineyl and 6-Triazol-yl of D- Glucitol Derivatives

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ARTICLE INFO

Received: 14 / 5 /2011
Accepted: 23 / 1 /2012
Available online: 30/10/2012
DOI: 10.37652/juaps.2012.62773

Keywords:
Synthesis ,
6-Aziridineyl ,
6-Triazol-yl ,
D- Glucitol Derivatives.

ABSTRACT

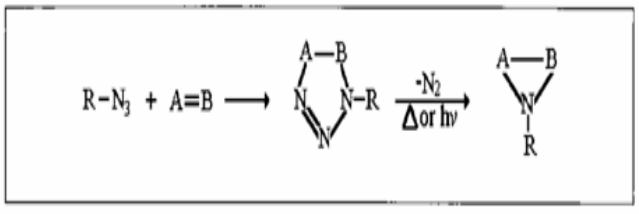
1,3 : 2,4 - Di - 0 -ethylidene - 5 -O - tosyl - 6 - (2 - cyano -1- aziridineyl) -6-deoxy-D- glucitol (4) , 6- (2- acetate -1- aziridineyl) derivative (5) and 6- (4-bromo methyl - 1,2,3- triazol -1-y1) (6) and the isomer (5- bromo methyl -1,2,3 - triazol-1-y1) derivative (7) were prepared from the mono tosylate mono azido derivative (3).Compound (3) underwent 1,3 - dipolar cycloaddition reactions with acrylonitrile and vinylacetate to give, the aziridine derivatives (4) and (5) via triazoline themolysis respectively, and with proprgyl bromide gave mixtuyre 1,2,3-triazol derivatives (6) and isomer (7).

Introduction:

Synthesis of alditol derivatives, especially those substituted at 1-or 6- or both positions have been prepared. These include; amino alditols1, 1,6- di-halogeno2, diazido3, mono azido4 and pyridyl amino5 derivatives.

Aldityl derivatives of hetrocyclic compounds(either one or two terminal carbon atoms of the alditol moiety bonded to a hetrocyclic) has also been synthesized using different approaches5,6

The intramolecular and intermolecular (3+2) dipolar cycloaddition reaction of organic azides with unsaturated compounds are well known7, to give triazole or triazoline ringis. However, application of this reaction in carbohydrate field has only been reported 8,9. Thermolysis of 1,2,3- triazolines produce the corresponding aziridines10.11and their photolysis gives aziridines12.The mechanism of triazoline thermolysis was discussed elsewhere13 .This mechanism shows that a loss of nitrogen gives aziridines:



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Certain 1,2,3-triazole derivatives have been reported to possess useful applications. Some are reported as fungicides and plant growth regulators14 as bactericides and medical fungicides 15 as insecticides and caricides16. The aziridine derivatives are said to possess anticancer and anticonvulsants17.

In continuation of our interest in synthesizing new 6-substituted position similar to those heving biological activity, we report in this worke the praparation of 6-aziridineyl (4), (5) and mixture 6- (1,2,3 - triazolyl) (6 + 7) derivatives of D- glucitol .

Results and Discussion:

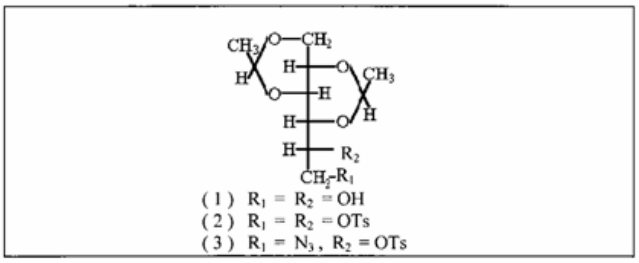
The 1,3 : 2,4 - di -0- ethylidene - D - glucitol(1) was selected as a starting material . due to the secondary hydroxyl group at position carbon - 5 and primary hydroxyl group at position carbon - 6 , the di -0- ethylidene derivative (1) was prepared from the reaction D-glucitol with paraldehyde in the process of hydrochloric acid18 . The reaction of (I) with P-toluene sulphonyl chloride in pyridine19at room temperature went smoothly to give the 5,6- ditosylate

derivative(2). The structure of (2) was analysis of i.r. spectral data .

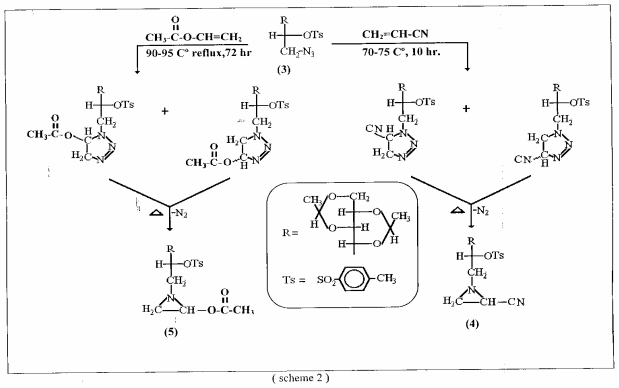
Treatment of(2) with sodium azide in dimethyl fon-namide20 with reflux for 10 min . give 1,3 : 2,4- di - 0 - ethylidene - 5 - 0 - tosyl - 6 - azido - 6- deoxy -D-glucitol (3) (scheme 1). The structure of which was assingened from the i.r. spectrum

which showed a strong absorption at 2115 cm -1 (N3) group and at 1370 , 1180 , 550 cm -1 (SO2) of the tosylate group. Unfortunately the tosylate group at C - 5 was difficult to replace and the reaction was not readily reproducible . The replacement of the secondary as well as the primary tosylate group although it was subsequenty found , to our surprise , that the 5 - 0 - tosylate group in (2) derivative could only be displaced with difficulty even in DMF. This is because a steric environment, the 3 - Oxygen being axial with respect to the 2,4 - 0 - ethylidene ring.

The (3 + 2) dipolar cycloaddition reaction of monotosyl monoazide derivative (3) with acrylonitrile and vinylacetate was carried out by fusion method. The thermolysis of triazoline gave aziridine derivatives (4) and (5).

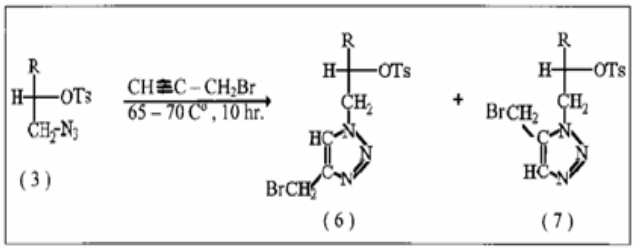


Scheme (1)



(scheme 2)

Simillarly when derivative (3) was heated with proprgyl bromide gave a mixture triazole 6 and 7 derivatives through 1,3 - dipolar cycloaddition reactions. Scheme (3) : The structures for the new compounds were assigned according to their i.r. spectral data and their elemental analysis (C.H.N) .



Scheme (3)

Experimental :

All solvents used were we parified by distilled, melting points were recorded on a status melting point instrument and are uncorrected. I R spectra were recorded on a Perken Elmer - 398 spectro photometer. Elemental analysis was performed using a Perkin - Elmer 240 B) instrument. Thin layer chromotography (TLC) were performed on a silica - gel F 254 (whatman) , and developed with the solvents mentioned , spots were visualized with iodine vapour. Column chromatography was silica - gel 40.

1,3 : 2,4 - Di -0 - ethylidene - 5 - 0- tosyl -6 - (2- cyano - 1- aziridineyl) - 6 - deoxy -D- glucitol (4):

The monotosyl mono azide (3) (1 gm , 2.4 mmol) was heated with acrylonitrile (0.77 gm , 14.5 mmol) on oil bath at (70 - 75) C° for 10 hr. The residue was purified by column chromatography on silica gel (Benzene : Diethyl ether 8:2) Rf 0.23 , to give pure amorphous aziridine (4) (0.48 gin , 43%) m.p (80 - 85) C° : I.R (KBr) 2240 Cm-1 (C=N) , 1270 Cm-1 (C=N), 1360 , 1175 , 550 Cm-1 (SO2).

Anal. for C20 H26 07N2S :

Calcd. : C, 54.79 ; H, 5.93 ; N, 6.39

Found : C, 54.90 ; H, 6.93 ; N, 6.20

1,3 : 2,4 - Di -0- ethylidene -5 - 0 - tosyl- 6-(2- acetate -1- aziridineyl) -6-deoxy -D-glucitol (5):

The derivative (3) (0.1 gm. , 0.2 mmol) was heated with vinyl acetate (0.2 gm , 2.3 mmol) for 72 hr. at (90 95) C° under reflux on oil bath The resulting solution was concentrated and the residue was purified by column chromatography on silica - gel (Benzene : Diethylether 8 : 2) Rf 0.07 to give syrupy product aziridine derivative (5) (0.08 gm, 80%). I.R (film) : 1730 Cm-I(C =O);1240 Cm-1 (C-O- C) ; 1360 , 1120 , 590 Cm-1 (SO2).

1,3:2,4 - Di -0- ethylidene - 5 -0 - tosyl - 6 - (4- bromo methyl -1,2,3- triazol - 1-y1) 6 - deoxy -D - glucitol (6) and isomer (5 - bromo methyl -1,2,3 - triazol - 1-yl) (7) :

The mono tosyl mono azide derivative (3) (1 gm, 2.4 mmol) was heated with proprgyl bromide (l gm, 8.7 mmol) on oil bath at (65 - 70) C° for 10 hr The resultant syrup was dissolved in chloroform and crystallized from petroleum ether (40- 60) C° to give mixture triazole (6 + 7) (1.1 gm, 85%) m.p(148 - 150) C° ; T.L.C : (Benzene : ether 8 : 2) Rf 0.15, 0.11:I.R(KBr):1600 Cm-I(C=C); 660 Cm-1 (C-Br) ; 1250 Cm-1(C - N) ; 1370 ,1170, 540 Cm-1 (SO2).

Anal. for C20 H26 07 N3 S Br. 2CHC13 : Calcd : C, 34.24 ; H, 3.63 ; N, 5.44 Found : C, 35.32 ; H, 3.52 ; N, 6.19

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P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
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تحضير مشتقات 6- ازردينيل و 6- ترايزوليل لـ - D- كلوسيتول

نبيل ياسين جمعة الهيتي وليد فرج حمادي وجيه يونس العاني

الخلاصة:

تم تحضير مشتقات 3,1 : 4,2 – ثنائي – O– ايثاليدين – 5 –O– توسيل–6– (2– سيانو –1–ازريدينيل) –6– ديوكسي – D – كلوسيتول (4) و 6– (2– اسيتيت –1– ازردينيل) (5) و 6 – (4– برومو مثيل –3,2,1– ترايزوليل) (6) وايزومره (5– برومو مثيل – 3,2,1– ترايزوليل) (7) من مشتق أحادي التوسيل احادي الأزيد (3) ومن خلال تفاعلات الاضافة ثنائية القطب 3,1– الحلقية تم مفاعلة المركب (3) مع كل من الاكريلونتريل واسيتات الفاينيل لنحصل عن طريق التحلل الحراري لمركبات الترايزولين الوسطية على مشتقات الأزردين (4) و (5) على التوالي . ومع المركب الاستيليني بروميد البروبرجيل لنحصل على مزيج مشتق 3,2,1– ترايزول (6) وايزومره (7).