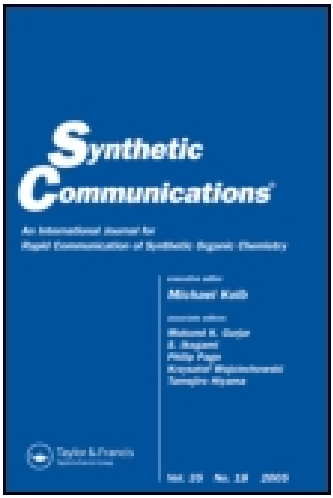

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MONTMORILLONITE K-10 CLAY CATALYSED GLYCOSIDATION OF 1-O- ACETYL-2,3-DIDEOXY -DL-PENT-2-ENOPYRANO-4-ULOSE

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Abstract: *The O-glycosidation reaction of 1- O- acetyl- 2,3-dideoxy- DL- pent-2- enopyran - 4 -ulose catalysed by the environmentally accepted and inexpensive industrial catalyst Montmorillonite K-10 clay with variety of alcohols in high yield is reported.*

The search for simple and efficient methods for glycosidation continues to be an area of active interest[1]. Glycosidation involving glycals, catalysed by 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone,[2,3] Tin (IV) chloride,[4] and Boron trifluoride diethyl etherate[5,6] have been exploited. During the course of some work on the cycloaddition of oxidopyrilium betaines derived from pyranulose acetates we observed that the later undergo glycosidation, albeit in low yield, with alcohols under the influence of Amberlite IR-120. It then occured to us that an ecofriendly clay catalyst such as montmorillonite K-10 might prove to be more efficient in promoting the glycosidation[7,8]of pyranulose acetates.

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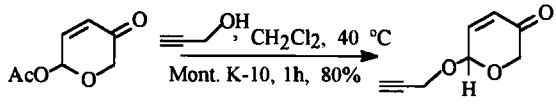
Herein we report a facile and high yielding glycosidation which involves the reaction of pyranulose acetate **1** with various alcohols **3-9** in the presence of catalytic amount of montmorillonite K10. The following example is illustrative (scheme 1).



1 **2a**

Scheme 1

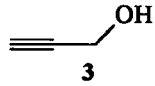
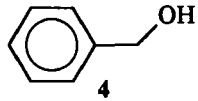
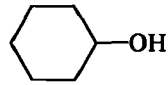
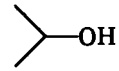
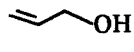
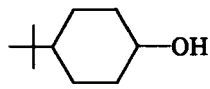
Treatment of **1** with propargyl alcohol **3** and 30% w/w montmorillonite K-10 in dry dichloromethane at 0-5 °C for 5 min. and then at 40 °C for 1h afforded the glycoside **2a** in 80% yield. The workup involves only filtration and evaporation of the solvent *in vacuo* . The recovered catalyst (Mont K-10) can be used twice without regeneration and the product yields are found to be the same. The IR spectrum of **2a** showed absorbance at 3300, 1685, 1640 cm^{-1} for acetylenic, enone carbonyl, and olefinic bond respectively. **2a** gave a molecular ion peak (M^+) at *m/z* 152 and a M+1 peak. Its ^1H NMR (90 MHz) shows peaks at δ 6.9 a doublet of doublet for H-2 proton, at δ 6.1 a doublet for H-3 proton , at δ 5.4 a doublet for H-1 proton, at δ 4.2 an ABq for H-5 methylene protons, and at δ 2.6 a triplet for ethylenic proton, and at δ 2.1 a singlet for methylene protons.

Similar results were obtained with a number of alcohols and these are summarised in table 1. In all cases the products were characterized by spectral data.

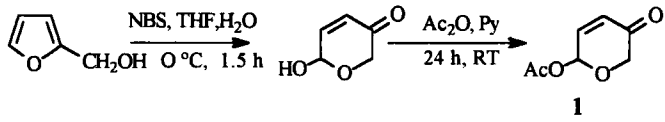
The pyranulose acetate **1** used in this reaction was conveniently prepared from furfuryl alcohol by the modification of a known procedure[9] (Scheme 2).

Table 1

Glycosidation reaction of **1** with alcohols catalysed by montmorillonite K-10 [a,b,c]

Entry	Alcohol[d]	Time (min)	Product[e]	Yield[f] (%)
1	 **3**	60	**2a**	80
2	 **4**	60	**2b**	74
3	 **5**	60	**2c**	92
4	 **6**	30	**2d**	85
5	*n* -Octanol **7**	60	**2e**	82
6	 **8**	55	**2f**	70
7	 **9**	45	**2g**	95

[a]:The montmorillonite K-10 was dried at 70 °C for 3h before each reaction. [b]: 30 % (w/w) Montmorillonite K-10 was used for each reaction. [c]: For conditions see experimental. [d]: 1.5 equivalents of alcohol was used for each case. [e]: The homogeneity of the compounds was established by chromatographic techniques and GCMS. [f]: Isolated yield after column purification.



1

Scheme 2

In conclusion, we have developed an efficient procedure for the glycosidation of pyranulose acetate which may be of wider application. It is noteworthy that the products of the reaction are potentially valuable building blocks for biologically active natural products[10] and synthons for a variety of deoxy sugars, which are constituents of antibiotics[11].

Experimental

The starting compound, pyranulose acetate **1**, was prepared by the modification of a reported procedure[9]. Dichloromethane was dried over P_2O_5. All the alcohols **(3-9)** were purified either by distillation or recrystallization. The Montmorillonite K-10 clay was purchased from Aldrich. IR spectra were recorded on a Perkin-Elmer model - 882 spectrophotometer. ^1H NMR (90 MHz) and ^{13}C NMR (22.4 MHz) spectra were recorded on a JEOL EX-90 spectrometer using TMS as internal standard and GCMS were recorded on a Fison - GC 8000 series Mass spectrometer.

Preparation of 6-hydroxy pyran-3(6H)-one[9b] **:**

A solution of furfuryl alcohol (2 g, 20.4 mmol) in THF:H_2O (4:1,40mL) at 0 °C was added NBS (4.7 g, 26.4 mmol) in small portions with constant stirring for about 1h. Then the solution was allowed to stir (0.5h) at the same temperature. The reaction mixture was extracted with ether (20mL X 4), and the ether layer was washed successively with 10% KI (5mL), 15% $Na_2S_2O_3$ (5mL), 10% sodium bicarbonate, saturated brine and dried over anhyd. Na_2SO_4. Evaporation of the solvent *in vacuo* at 35 °C afforded the 6-

hydroxy pyran-3(6H)-one which was used for the next step without further purification.

***Preparation of pyranulose acetate* 1 :**

Acetic anhydride (4mL) was added to the crude 6-hydroxy pyran-3(6H)-one and catalytic amount of pyridine (3drops) at 0 °C. The solution was allowed to stirr 0.5h at the same temperature and then 24h at room temperature. The reaction mixture was then neutralised with saturated sodium bicarbonate and extracted with dichloromethane (25mL X 2). The organic phase was washed with sat. $CuSO_4$(5mL), water (5mL), and saturated brine and dried over anhyd. Na_2SO_4. Evaporation of the solvent *in vacuo* at 50 °C afforded a thick brown mass which upon column purification (silica gel) with 5% ethyl acetate - hexane mixture afforded pyranulose acetate **1** as colourless oil which crystallized on standing. [m.p. 41-43 °C; Lit.[9] 41-45 °C]

Typical experimental procedure for glycosidation:

***Synthesis of* 2(a-g)**

A mixture of **1** (500 mg, 3.2mmol) and **3** (265mg, 4.8 mmol,1.5equiv) in dry CH_2Cl_2 was cooled in an ice bath and montmorillonite K-10 (150 mg, 30 % w/w) was added to it. The mixture was allowed to stir for about 5 min. at the same temperature and then at 40 °C until TLC shows the absence of starting material (*ca.* 1h). The reaction mixture was filtered and concentrated *in vacuo.* Purification of the crude material by chromatography on a short column (silica gel, 100-200 mesh); rapid elution with 5% hexane : ethyl acetate afforded 390 mg **2a** in 80% as a colourless oil.

***Spectral data for 1- O - propargyl- 2,3- dideoxy -DL- pent- 2- enopyrano - 4 - ulose* 2a:**

Compound nature : low melting solid : T.L.C homogeneous (R_f : 0.4 Hexane: EtOAc 95:5); IR (CCl_4, cm $^{-1}$) : 1680 (enone carbonyl), 1620(double bond),

3300 (acetylenic C-H); ^{1}H NMR ($CDCl_3$ / TMS ; 90 MHz) : δ 2.1 (s, 2H, *methylene protons*), 2.6(t, 1H, -C≡C-*H*), 4.2 (ABq, 2H, *H*-5), 5.4(d, 1H, *H*-2), and 6.1(d, 1H, *H*-3), 6.9 (dd, 1H, *H*-1); ^{13}C NMR ($CDCl_3$ / TMS ; 22.4 MHz) : δ 70, 81, **90**, **93**, 107, 143, 158, 208. GCMS *m/z*: 197 (M^++1), 196 (M^+), 195 (M^+-1), 166, 97, 84.

***Spectral data for 1- O - cyclohexyl - 2,3- dideoxy -DL- pent- 2- enopyrano - 4 -ulose* 2c:**

Compound nature : low melting solid : T.L.C homogeneous (R_f : 0.4 Hexane: EtOAc 95:5); IR (CCl_4, cm $^{-1}$) : 1680 (enone carbonyl), 1620(double bond); ^{1}H NMR ($CDCl_3$ / TMS ; 90 MHz) : δ 1.3- 2.1 (m, 11H, *methylene protons*), 4.2(ABq, 2H, *H*-5), 5.2 (d, 1H, *H*-1), 6.1 (d, 1H, *H*-3), and 6.8 (dd, 1H, *H*-2); ^{13}C NMR ($CDCl_3$ / TMS ; 22.4 MHz) : δ 38, 40, 47, 49, 81, 92, 106, 111, 143, 159, 209. GCMS *m/z*: 197 (M^++1), 196 (M^+), 195 (M^+-1), 166, 97, 84.

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