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Clay Montmorillonite in Carbohydrates : Use of 'Claysil' as an Efficient Heterogenous Catalyst for the Intramolecular Ferrier Reactions leading to 1,6-anhydro rare Saccharides[§]

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Abstract : Clay montmorillonite supported silver reagent - claysil - was prepared and advantageously used in the intramolecular Ferrier reaction of 6-hydroxy glycals la-9c. The unsaturated sugars l3a-2lc so obtained were stereoselectively hydroxylated leading to the rare l,6-anhydro saccharides 22a-30c. Synthesis of (D)-allosan (31) and (D)-gulosan (34) is described.

Acid catalysed organic transformations by use of clay montmorillonite¹ as 'solid acid'² in liquid phase is an area of immense importance, which prompted us to investigate its utility as a catalyst in intramolecular Ferrier (IMF) reactions. Herein, we describe, for the first time the preparation of 'claysil' - a clay montmorillonite supported silver reagent - and demonstrate its use and advantages in rare IMF reaction of 6-hydroxy glycals **la-9c** to obtain **l**,6-an-hydro sugars **l3a-2lc**, which in turn were hydroxylated to **l**,6-anhydro saccharides **22a-30c** that are hitherto difficult to synthesise.

Ferrier^{3,4} and IMF^5 reactions were conventionally carried out by the use of Lewis acids such as $SnCl_4$, $TiCl_4$, BF_3 . Et_2O etc. as catalysts, whereas by use of 'claysil' as a supplimentary catalyst, the IMF reactions were catalyzed much more effectively; the advantages being a) low cost and high "stability" b) rapid reaction "rate" and c) simple and easy work up procedures.



The requisite 6-hydroxy glycals 1a-9c were prepared by known⁶ procedures. In the first instance 6-O-silyl protected glycal 10 was subjected to IMF reaction with clay montmorillonite K-10 (Fluka) in CHCl₃ (50°C, 18 h) to afford an inseparable mixture of 13a and 35 alongwith some unidentified products in poor yield, whereas 6-hydroxy glycal 1a in 10 h gave 13a and 35 (5:2) in 30% yield. Under identical conditions 'clay-Hg' catalysed IMF reaction on 10 gave 13a and 35 (12 h) in 40% yield (4:1), while 1a in 8 h gave 13a as a sole product in 60% yield. However, reaction of 1a was smoothly catalysed by 'claysil' in 2 h to afford 13a as an exclu-

sive product in 80% yield unlike 10, which gave 13a in 8 h (60%). Thus, the above study amply demonstrated the efficacy and superiority of 'claysil' as the suitable catalyst and the 6-hydroxy glycals 1a-9c instead of 6-O-silyl glycals 10-12 as the suitable substrates for these reactions. The glycals 1a-6c and the disaccharide glycals 7a-9c having sensitive inter-glycosidic linkages, were transformed into 1,6-anhydrosugars 13a-21c in high yield (80-85%) and characterised by 1 H and 13 C NMR spectra.



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Further, 13a-21c were subjected to stereoselective <u>cis</u>-hydroxylation⁷ (OsO₄, pyridine) to afford the rare 1,6-anhydro saccharides 22a-27c and disaccharides 28a-30c in high yield (62-85%), which are otherwise made by a lengthy sequence of reactions in poor yields. The high stereoselectivity realised in 22a-30c was defined by the rigidity of [3.2.1] bicyclic system present in the unsaturated sugars 13a-21c. Accordingly, 14b on osmylation and debenzoylation gave (D) allosan⁸ 31 [α]_D -70 (c 0.6, H₂O), lit.⁹ [α]_D -75.8 (c 0.6, H₂O) and was characterised

Glycal	Catalyst	Time (h)	Product(s)	Yield(s)
<u></u>	<u> </u>	·		
10	Claymont. K-10	18	1 3 a, 35	Poor
la	-do-	10	-do-	30
10	Clay-Hg [¶]	12	-do-	40
la	-do-	8	13a	60
10	Claysil [¶]	8	13a	60
la	-do-	2	-do-	80

Table

- ¶ 'Clay-Hg' and 'Claysil' were prepared from $Hg(NO_3)_2$ (2.5 g) and/or $AgNO_3$ (2.5 g) and clay montmorillonite K-10 (5 g) in 50 ml H₂O. Filtered, washed with water and dried at 120°/10 mm for 12 h.
- An oven dried round bottom flask charged with glycal (1 mmol) and catalyst (0.1 g) in CHCl₃ (10 ml) was heated at 50°C under N₂ atmosphere. After completion of reaction, it was filtered through a pad of celite, washed with CHCl₃ and evaporated to give the products after chromatographic purification.

as its tri-O-acetyl derivative 32, $[\alpha]_D$ -70.0 (c 1.0 CHCl₃), lit.⁹ $[\alpha]_D$ -70.8 (c 1.0, CHCl₃), likewise 17b on osmylation and benzoylation gave 33 $[\alpha]_D$ +213 (c 0.5, CHCl₃), lit.¹⁰ $[\alpha]_D$ +214 (c 2.0 CHCl₃), debenzoylation of which gave (D)-gulosan 34 $[\alpha]_D$ +51.4 (c 0.5, H₂O), lit.¹⁰ $[\alpha]_D$ +50.4 (c 2.8, H₂O).

'Claysil' thus may find a wide variety of applications in organic synthesis with a special reference to carbohydrates.

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References

1. Laszlo, P.; Acc. Chem. Res., 1986, 19, 121; Laszlo, P. Science, 1987, 235, 1473; Thomas,

J.M. and Theocharis, C.R. 'Modern Synthetic Method', Vol. 5, Scheffold, R. Ed. Springer-Verlag, Berlin, 1989, 249.

- 2. Onaka, M.; Hosokawa, Higuchi, K. and Izumi, Y. Tetrahedron Lett. 1993, 34, 1171.
- 3. Ferrier, F.J. Adv. Carbohydr. Chem. Biochem., 1969, 199; Ferrier, F.J. and Prasad, P. J. Chem. Soc. C., 1969, 570.
- 4. Lundt, I. and Pedersen, C. Acta. Chem. Scand., 1970, 24, 240; Descotes, G. and Martin, J.C. Carbohydr. Res., 1977, 56, 168; Grynkiewicz, G.; Priebe, W. and Zamjski, A. Carbohydr. Res., 1979, 68, 33; Hadfield, A.F. and Satorelli, A.C. Carbohydr. Res. 1982, 101, 240.
- 5. Mereyala, H.B.; Ramanaiah, K.C.V. and Dalvoy, V.S. Carbohydr. Res., 1991, 225, 151.
- 6. Mereyala, H.B. and Ramanaiah, K.C.V. J. Chem. Soc., (S) 1991, 197.
- Brimacombe, J.S.; Hanna, R.; Kabir, A.K.M.S.; Bennett, F. and Taylor, I.D. J. Chem. Soc. Perkin. Trans I, 1986, 815; Cha, J.K.; Christ, W.J. and Kishi, Y. Tetrahedron Lett. 1983, 24, 3943, 3947.
- 8. Matsumoto, M.; Ebata, T.; Koseki, K.; Kawakami, H. and Matsushita, H. Heterocycles, 1991, 32, 2225.
- 9. Pratt, J.W. and Richtmyer, N.K. J. Am. Chem. Soc. 1955, 77, 1906.
- 10. Stewart, L.C. and Richtmyer, N.K. J. Am. Chem. Soc. 1955, 77, 1021.
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