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MONTMORILLONITE CLAY CATALYSIS I: AN EFFICIENT AND CONVENIENT PROCEDURE FOR PREPARATION OF 5(6)/5'(6')-UNSATURATED 3β,3'β-DISTERYL ETHERS

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Abstract: In the presence of montmorillonite K 10, 5(6)-unsaturated sterols (**1**) were heated at refluxing temperature in dichloromethane to provide 5(6)/5'(6')-unsaturated 3β,3'β-disteryl ethers (**4**) in 69-73% yield. The mechanism of the reaction was discussed.

Under some conditions disteryl ethers are formed by dehydration of sterols, e.g. cholesterol, stigmasterol and sitosterol[1-6]. They are also detected from the industrial refining of fats and oils where they are presumably formed by the action of acidic bleaching earth on sterols which are minor constitutents of fats and oils[7-9]. Therefore, the detection of disteryl ethers in fats and oils may be useful as evidence of industrial bleaching[10,11].

In a current research of our simulation of diagenesis of natural sterols under acidic clay minerals, disteryl ethers are proposed to be very early diagenetic intermediates of sterols. Consequently, a series of disteryl ethers are required for this study. Numerous publications describe the formation of disteryl ethers during various chemical reactions of sterols[1-6], but in a view point of synthesis none of those

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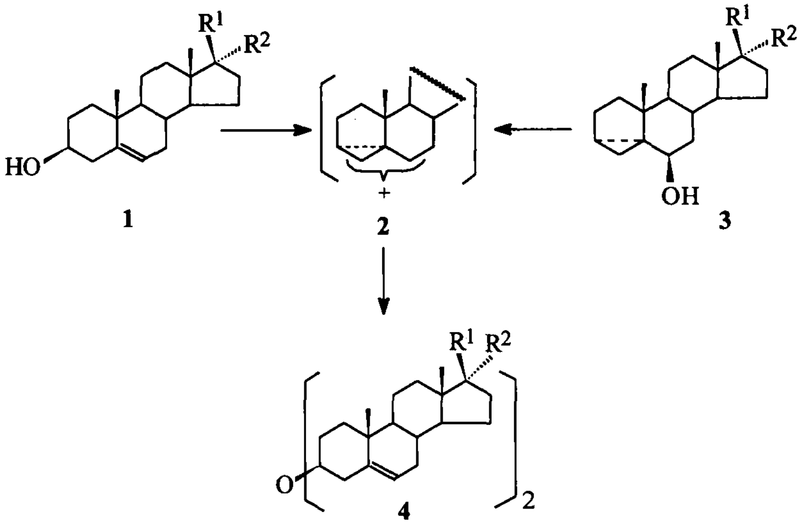
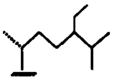
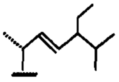
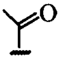


Scheme

Table. Formation of disteryl ethers from sterols catalysized by montmorillonite K 10

Entry	R^1	R^2	Reaction time(h)	Product	Isolated yield(%)	mp(°C)
1a		H	6	4a	73	200-203 197-200[6]
1b		H	13	4b	72	192-194 192-194[6]
1c		H	8	4c	69	206-209 208-210[6]
1d		H	12	4d	71	225-227
1e	R^1R^2=O		11	4e	70	272-274
3a			12	4a	69	200-203

method gave satisfactory results either due to low yield or the reagent was not readily available[4]. The spectroscopic data of some disteryl ethers were also reported[6].

Montmorillonite, a class of acidic clays, have been widely used in organic synthesis[12-19] due to their readily available, ease of set up and of work up, mild experimental condition and high yield and/or selectivity. We wish to report here an efficient and convenient procedure for preparation of 5(6),5'(6')-unsaturated 3β,3'β-disteryl ethers catalysized by montmorillonite K 10.

As shown in Table, in the presence of montmorillonite K 10, several side chain varied sterols (**1a**-**1e**) were heated at refluxing temperature in dichloromethane for 6-13 h to give corresponding disteryl ethers (**4a**-**4e**) in 69-73% yield. The configuration of C-3 in the products **4** was complete retention as indicated by ^{1}H and ^{13}C NMR spectra. We have also reacted cholest-5-en-3α-ol (**5**), 5α-cholestan-3β-ol (**6**), ergosterol (**7**) and vitamin D_2 (**8**) in the same conditions as **1** for 10 h, but none of these reactions gave the proposed disteryl ethers. 5α-Cholestan-3β-ol (**6**) mainly provided backbone rearranged cholestenes as reported[20]. In the other three cases, cholest-5-en-3α-ol (**5**), ergosterol (**7**) and vitamin D_2 (**8**) remained unchanged. Further, 3α,5-cyclo-5α-cholestan-6β-ol (**3a**) gave **4a** (69%) and **1a** (5%). These results suggested that disteryl ethers **4** were produced through the same carbonium intermediate **2** from **1** and **3** (Scheme). This was also supposed by literature[4]. 3α-Hydroxy is not an easily leaving group as it occupies an axial position in **5**. The conjugated double bonds in **7** and **8** prevent their formation of carbonium **2**.

In conclusion, we provided an efficient and convenient method for preparation of 5(6)/5'(6')-unsaturated 3β,3'β-disteryl ethers.

Experimental

Melting points were uncorrected. Elemental analysis were performed on a PE-2400 instrument. IR spectra were recorded on a PE-983G as liquid films. ^{1}H and ^{13}C

NMR spectra were measured on a Bruker AM-400 or on a Bruker AC-80 spectrometer (TMS, $CDCl_3$). Mass spectra were determined on a VG-7070E spectrometer (EI, 70 eV). Montmorillonite K 10 was purchased from Fluka and dried at 100°C for 1 h prior to use.

General procedure: A mixture of sterol (**1**, 1.00 mmol) or 3α,5-cyclo-5α-cholestan-6β-ol (**3a**, 386 mg, 1.00 mmol), montmorillonite K 10 (400 mg) in dichloromethane (20 mL) was heated under stirring at refluxing temperature for 6-13 h as indicated in Table till the the substrate was disappeared (TLC). After cooling, the catalyst was removed by filtration and the solvent was evaporated under reduced pressure to give a light yellow solid. The crude product was chromatographied on silica (200-300 mesh), eluted with petroleum ether (b.p. 60-90°C) or the mixture of petroleum ether and diethyl ether to afford crystalline disteryl ether **4**. The melting points and ^1H NMR data of **4a**, **4b** and **4c** agreed well with those reported[6] (Table).

4d: mp 225-227°C (colorless needles from acetone); $C_{42}H_{62}O_3$ required C: 82.03%, H: 10.16%, found C: 82.13%, H: 10.17; ν_{max} 2940, 1700, 1456, 1352, 1095cm^{-1}; δ_H(80 MHz) 0.63(6H, s, 18,18'-H_6), 1.00(6H, s, 19,19'-H_6), 2.12(6H, s, 21,21'-H_6), 3.29(2H, m, 3α,3'α-H_2), 5.35(2H, d, J=4 Hz, 6,6'-H_2)ppm; δ_C(100 MHz) (number of carbon) 13.18(18), 19.34(19), 21.03(11), 22.77(15), 24.45(21), 29.35(2), 31.50(12), 31.60(7), 31.60(8), 36.62(10), 37.37(1), 38.61(16), 39.95(4), 43.96(13), 50.06(9), 56.70(14), 63.67(17), 76.22(3), 121.02(6), 141.25(5), 209.48(20)ppm; m/z (%) 614(M^+, 2.4), 449(0.7), 364(1.9), 314(48), 299(100), 298(100), 281(67), 161(77), 149(62), 121(51).

4e: mp 272-274°C (colorless plates from acetone); $C_{38}H_{54}O_3$ required C: 81.67%, H: 9.74%, found C: 81.62%, H: 9.83%; ν_{max} 2940, 1733, 1452, 1372, 1095cm^{-1}; δ_H(400 MHz) 0.894(6H, s, 18,18'-H_6), 1.037(6H, s, 19,19'-H_6), 3.299(2H, m, 3α,3'α-H_2), 5.376(2H, d, J=5.0 Hz, 6,6'-H_2)ppm; dC(100 MHz) 13.48(18), 19.35(19), 20.27(11), 21.61(15), 29.25(2), 30.76(12), 31.37(7), 31.42(8), 35.76(16), 36.90(10), 37.75(1), 39.97(4), 47.48(13), 50.26(9), 51.70(14), 76.15(3), 120.55(6), 141.42(5), 221.03(17); m/z (%) 558(M^+, 0.4), 327(0.3), 286(28), 271(100), 253(24), 175(9), 161(12), 147(12), 119(14), 105(20).

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