

## Chemical Conversions using Sheet Silicates: Novel Intermolecular Dehydrations of Alcohols to Ethers and Polymers

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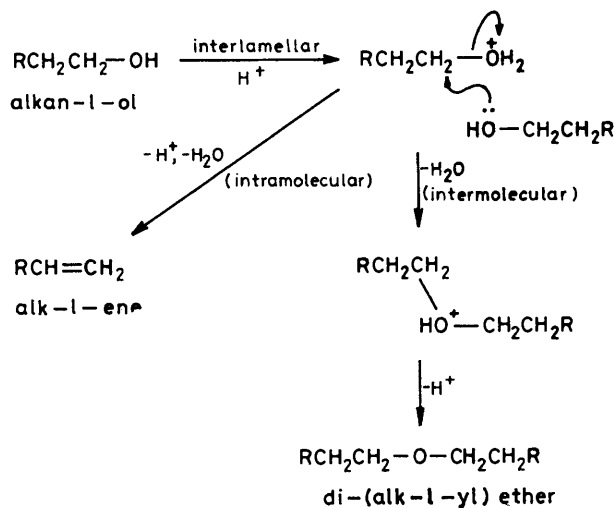
**Summary** Aliphatic primary alcohols, when intercalated in certain ion-exchanged montmorillonites, react preferentially *via* an intermolecular nucleophilic displacement of water to give high yields of di-(alk-1-yl) ethers, rather than the competitive intramolecular dehydration to alkenes; an essentially similar process yields polymeric material, poly(phenylenemethylene), from benzyl alcohol, but aliphatic secondary and tertiary alcohols, in contrast, yield alkenes almost exclusively.

We have recently shown<sup>1,2</sup> that the interlamellar region of ion-exchanged montmorillonites provides a microenvironment which facilitates addition of an intercalated water molecule to two molecules of an alk-1-ene to give a di-(alk-2-yl) ether. We subsequently established that alk-1-enes can add directly to intercalated carboxylic acids to give esters,<sup>3</sup> the montmorillonite acting as a protonic catalyst, in contrast with the situation in the earlier example where the intercalated water was used up in the reaction with the eventual collapse of the sandwich structure of the solid.

We have since established<sup>4</sup> that alkan-1-ols react with ion-exchanged montmorillonites, under a variety of conditions, to produce both di(alk-1-yl) ethers and alkenes. Typical product yields are shown in the Table.

The reactions were carried out mainly in small stainless steel pressure vessels (*ca.* 20 cm<sup>3</sup> capacity) and a typical charge was 0.5 g of solid catalyst and 5 g of reactant. The pressure vessel was immersed in a liquid thermostat capable of operating up to 220 °C.

The alkenes are presumably produced by simple proton-catalysed dehydration, but the production of the di-(alk-1-yl) ethers must involve an intermolecular coupling reaction. The fact that primary ethers are produced in such predominance must preclude the intermediacy in their formation of either carbocations or alkenes as these would result in the predominant production of the secondary ethers.<sup>1-3</sup> We are led to the conclusion that catalysis takes place by protonation of the alkan-1-ol in the interlamellar zone, followed by nucleophilic displacement of water by a neighbouring unprotonated alkan-1-ol molecule (Scheme 1).



SCHEME 1

TABLE. Product distribution (weight %) for reactions of alcohols with Al<sup>3+</sup>-exchanged montmorillonite at 200 °C; reaction time 4h.

Reactant	Recovered reactant	Ethers			Alkenes	Alkene dimers
		1,1-	1,2-	2,2-		
<b>Primary alcohols</b>						
Ethanol	35	64	—	—	—	1
Propan-1-ol	22	63	8	—	3	4
Butan-1-ol	44	45	4	—	6	1
Pentan-1-ol	46	32	5	—	12	5
Hexan-1-ol	38	41	5 <sup>a</sup>	—	14	2
Heptan-1-ol	50	39	1.5 <sup>a</sup>	—	9	0.5
Octan-1-ol	59	30	—	—	11	1
3-Methylbutan-1-ol	25	58	—	—	4	13
<b>Secondary alcohols</b>						
Propan-2-ol	29	—	—	30	40	1
Butan-2-ol	10	—	—	9	78	2
Pentan-2-ol	9	—	—	7	83	1
Hexan-2-ol	7	—	—	5	82	6
Cyclohexanol	6	—	—	4	88	1
<b>Tertiary alcohols</b>						
2-Methylpropan-2-ol	3	—	—	—	18	79 <sup>b</sup>
2-Methylbutan-2-ol	2	—	—	—	93	4

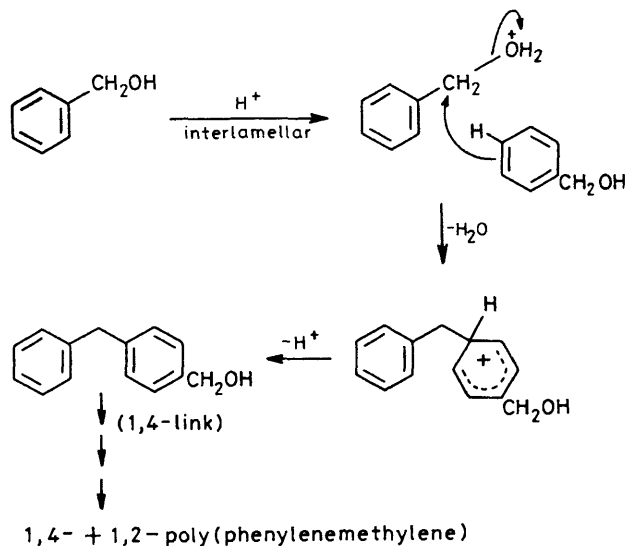
<sup>a</sup> Contains a small proportion of 1,3-ether. <sup>b</sup> 50% dimer + 29% tetramer.

Small quantities of alk-1-yl alk-2-yl ethers and trace amounts of alk-1-yl alk-3-yl ethers were observed in the product mixtures and these presumably arise from secondary processes. Further, secondary products from alkene isomerisation and dimerisation were also observed and were typical of those found in the proton-catalysed reactions of alkenes already described.<sup>1,3</sup>

Reaction of aliphatic secondary alcohols with ion-exchanged montmorillonites yielded only small quantities of the di-secondary ethers but gave high yields of the corresponding alkenes *via* competitive dehydration (Table); also, the tertiary aliphatic alcohols yielded exclusively alkenes and their oligomers. Propan-2-ol was found to be an exception to this generalisation as moderate quantities of both the di-(alk-2-yl) ether and alkene were produced in this case.

Benzyl alcohol furnished a polymeric material as the only product from treatment with Al<sup>3+</sup>-exchanged montmorillonite at 200 °C. The polymer was totally soluble in both cold benzene and chloroform and the <sup>1</sup>H n.m.r. spectrum established the presence only of equivalent aromatic protons and methylene-bridge protons. The chemical shifts indicated that all of the oxygen functions had been removed and that the compound was a new polymer, poly(phenylenemethylene), the structure of which is consistent with the observed mass spectra fragmentations. Analysis of the molecular-weight distribution by gel permeation established that the greater part of the material had a molecular size in the range 10–100 molecular units, centering on 20 units, with two further, satellite, distributions (*ca.* 25% w/w) centering on about 650 and 2500 molecular units. The data suggested that both *p*- and *o*-couplings were present.

The probable mechanism for the formation of this type of polymer is illustrated in Scheme 2 and is the result of interlamellar protonation followed by nucleophilic displacement of water by the reactive *o*- and *p*- positions of a neighbouring ring. Further protonation and coupling would give the polymer.



SCHEME 2

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