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# Reactions of Alcohols with Alkenes over an Aluminum-Exchanged Montmorillonite

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**Abstract:** The reaction of 2-methyl pent-2-ene with primary alcohols ( $C_1$ - $C_{18}$ ) at  $95^\circ C$  over an Al-montmorillonite gave yields of 20– 90% of ethers of the type  $R-O-C(CH_3)_2C_3H_7$ . Lower yields were produced if secondary alcohols were employed, and tertiary alcohols gave only a trace of this ether. When a variety of alkenes was reacted with butan-1-ol at  $95^\circ C$  over a similar catalyst, no reaction occurred unless the alkene was capable of forming a tertiary carbonium ion immediately upon protonation. In this case the product was the tertiary ether  $t-R-O-nC_4H_9$ . However, at a reaction temperature of  $150^\circ C$  a variety of products were formed including (1) ether by the attack of butanol on the carbonium ions produced either directly from protonation of the alkenes or by hydride shift from such an ion, (2) alkenes by the attack of  $n-C_4H_9^+$  ions (derived from protonation and dehydration of butanol) on the alkene, (3) di-(but-1-yl) ether by dehydration of the butanol, and (4) small amounts of alcohol by hydration of the alkene. The differences in reactivity below and above  $100^\circ C$  are related directly to the amount of water present in the interlayer space of the clay and the degree of acidity found there. Although the clay behaves as an acid catalyst, the reactions are far cleaner (more selective) than comparable reactions catalyzed by sulfuric acid.

**Key Words:** Alcohol • Alkene • Aluminum • Catalyst • Montmorillonite

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