

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°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°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°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°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.

INTRODUCTION

An extensive study has been made of a wide range of organic reactions catalyzed by clay minerals (see, e.g., Fripiat and Cruz-Cumplido, 1974; Theng, 1974; Thomas *et al.*, 1977; Bittles *et al.*, 1964a, 1964b, 1964c). Recently, renewed interest has been shown in the use of natural and synthetic smectitic clays as highly selective acid catalysts (e.g., Adams *et al.*, 1978, 1979a, 1979b; Ballantine *et al.*, 1981a, 1981b). In many studies carbonium ions, formed by the protonation of the reactant molecules, have been considered to be essential intermediates in the reactions. The protons originate from the dissociation of interlayer water molecules coordinated to the exchangeable cations (Mortland, 1968; Fripiat and Cruz-Cumplido, 1974)—indeed the interlayer water in smectites is known to be dissociated to a much greater extent than bulk water (Hougardy *et al.*, 1976; Mortland *et al.*, 1963; Fripiat *et al.*, 1965; Touillaux *et al.*, 1968).

At low temperatures (<100°C) the reactions of alkenes over montmorillonites usually produce ethers or alcohols, depending upon the type of alkene (Adams *et al.*, 1979a, 1982a), whereas at higher temperatures they give dimers and other oligomers. Recently, Ballantine *et al.* (1981b) found that the reactions of alcohols with ion-exchanged montmorillonites give di-(alk-1-yl) ethers at 180°C. The possibility of reaction between alcohols and alkenes over ion-exchanged montmorillonite catalysts has been explored in the case of methyl t-butyl ether (MTBE) production from isobutene and methanol

(Bylina *et al.*, 1980; Adams *et al.*, 1982b) or t-butanol and methanol (Adams *et al.*, 1981).

In the present study we have extended this work to the reactions of a range of alkenes and alcohols at temperatures both above and below 100°C. Initially the alkene chosen was 2-methyl pent-2-ene, which is similar to isobutene in that protonation should give a tertiary carbonium ion. In addition, this alkene is much easier to handle than isobutene and reaction with a range of alcohols was attempted. A variety of alkenes was also reacted with butan-1-ol. In all experiments an Al-exchanged montmorillonite was used as a catalyst, because this material is highly acidic (Mortland, 1968).

EXPERIMENTAL

Catalyst characterization

The Wyoming bentonite used in this study (Volclay, foundry grade, Hopkin and Williams Ltd.) was crushed, separated from gross impurities and size graded in a cyclone before delivery. Eighty-five percent of the particles were specified as being <75 μm . The <2- μm clay fraction was selected by sedimentation. Cation exchange was carried out by exposing the clay to a 0.6 mole/liter solution of $Al(NO_3)_3 \cdot 9H_2O$ for 24 hr. The clay was then centrifuged and resuspended in deionized water repeatedly until a test for the exchanging salt proved negative, after which the clay was isolated by centrifugation, dried in an oven at 40°C, and ground finely. The cation-exchange capacity (CEC) of the isolated montmorillonite sample was found to be 70 ± 2 meq/100 g for air-dry material by a precipitation method described previously (Adams *et al.*, 1981) and also by

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the conductimetric method of Mortland and Mellor (1954). These exchange capacities correspond to $1/6 \text{ Al}^{3+}$ per Si_8O_{20} unit.

For all experiments pre-weighed Al-exchanged samples were equilibrated for 36–48 hr over a saturated LiCl solution at 30°C ; this salt solution produces an atmosphere of constant 12% RH and consistently gave a fixed water content in the interlamellar space of the clay. The reproducibility of the clay water content is important because the acidity of interlayer water is a function of the amount of such water present (Mortland, 1968), and the product of reactions catalyzed by montmorillonites have likewise been shown to be dependent upon this content of water (e.g., Adams *et al.*, 1979a). Thermogravimetric analysis showed that the clay samples contained 4.2×10^{-3} moles $\text{H}_2\text{O}/\text{g}$ clay, i.e., 3.0 water molecules/unit cell.

Gas-liquid chromatography and mass spectrometry

Gas-liquid chromatography (GLC) was used to monitor the purity of reactants and to analyze the reaction products. Glass columns, 0.25-inch internal diameter, were packed with 10% polyethylene glycol 20 M, with 2% silver nitrate supported on acid-washed silanized Chromosorb G. For the identification of reaction products a gas-liquid chromatograph coupled to an AEI MS 30 mass spectrometer was used with a DS 50 S micro-processor.

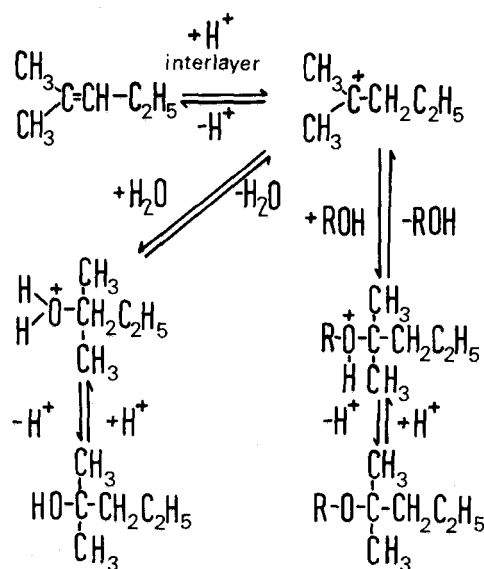
Reaction conditions

Teflon-lined brass vessels were employed for the reactions carried out at 95°C ; stainless steel vessels were used at 150°C . These containers were charged with either 1.0 g or 0.5 g (12% RH) of Al-exchanged clay together with the appropriate alkene and alcohol and *n*-hexane solvent. The vessels were sealed, placed in thermostatted oil baths, and stirred magnetically.

RESULTS

Reaction of 2-methyl pent-2-ene with alcohols

Reactions of 2-methyl pent-2-ene were carried out in Teflon-lined vessels at 95°C for 5 hr with 1 g of Al-clay (12% RH) and 12.5 mmole of the pentene and the appropriate alcohol; 3 cm^3 of *n*-hexane was used as solvent. Reasonable yields (20–40%, Table 1) of *t*-ether, i.e., 2-alkoxy 2-methyl pentane, were obtained by the acid-catalyzed reaction of 2-methyl pent-2-ene with all straight-chain alcohols (Figure 1) with carbon chain lengths from C_2 to C_{18} . With methanol the reaction was much more efficient and a larger ($\sim 90\%$) yield was observed. Here a small quantity of 2-methyl pentan-2-ol was produced from the hydration of the parent alkene, and a small quantity of MeOMe was formed from the methanol; as was found previously in the formation of



2-methyl pentan-2-ol

2-methyl-2-alkoxy pentane

Figure 1. Mechanism for the acid-catalyzed reaction of 2-methyl pent-2-ene with alcohols (Al-montmorillonite catalyst).

methyl *t*-butyl ether when using a clay catalyst (Bylina *et al.*, 1980; Adams *et al.*, 1981b). At this temperature methanol is the only alcohol to form a di-alkyl ether, whereas Ballantine *et al.* (1981b) showed that at higher temperatures di(alk-1-yl) ethers can be synthesized from *n*-alcohols using clay catalysts.

The ethers produced were identified by GLC-MS cracking patterns. Generally the yield of the tertiary alcohol, 2-methyl pentan-2-ol, was between 0.8 and 1.2 mole, which is less than that which could have been produced if all of the interlayer water originally in the clay had been consumed (4.2 mmole). No dimers of 2-methyl pent-2-ene were found in any reaction at 95°C , whereas in a comparable reactions involving methanol and 2-methyl propene, Adams *et al.* (1982b) reported the production of dimers of the reactant alkene. Where secondary alcohols were used as reactants, the yield of the appropriate tertiary ether was less than with primary alcohols, and a tertiary alcohol led to a negligible yield of ether.

These results indicate that there is no limit to the size of *n*-alcohols that can react to give *t*-ethers (up to C_{18}); the lower yields obtained with secondary and tertiary alcohols are probably due to the increase in steric hindrance around the hydroxyl group which prevented the tertiary carbonium ion (produced by protonation of the alkene) and the alcohol from approaching each other in a manner suitable for ether formation. The yield of 2-methyl pentan-2-ol is greater when secondary or tertiary alcohols are used rather than primary alcohols because the ether formation is restricted by steric hindrance; there are, therefore, more protonated al-

Table 1. Yields of tertiary hexyl ethers (R-O-C(CH₃)₂C₃H₇) and the tertiary alcohol 2-methyl pentan-2-ol using various alcohols.¹

Alcohol (ROH)	R-O-C(CH ₃) ₂ C ₃ H ₇ /mmole	2 methyl pentan-2-ol/mmole
CH ₃ OH	11.3 ²	1.2
C ₂ H ₅ OH	3.0	0.8
n-C ₃ H ₇ OH	3.5	0.8
n-C ₄ H ₉ OH	4.8	1.1
n-C ₅ H ₁₁ OH	3.7	0.75
n-C ₆ H ₁₃ OH	3.8	0.9
n-C ₄ H ₁₅ OH	3.9	0.8
n-C ₈ H ₁₇ OH	4.7	1.1
n-C ₉ H ₁₉ OH	4.0	0.4
n-C ₁₀ H ₂₁ OH	3.7	1.0
n-C ₁₂ H ₂₅ OH	3.3	0.9
n-C ₁₄ H ₂₉ OH	3.2	1
n-C ₁₆ H ₃₃ OH	2.5	1
n-C ₁₈ H ₃₇ OH	2.4	1
CH ₃ CH(OH)CH ₃	0.71	1.87
CH ₂ -CH ₂ -CHOH	0.86	1.1
(CH ₂) ₃ COH	0.07	2.6

¹ 1 g Al-clay (12% RH) + 12.5 mmole 2 methyl pent-2-ene + 12.5 mmole ROH + 3 cm³ n-hexane (5 hr, 95°C).

² This value is based on the loss of methanol and gives the total of this ether and a small amount of MeOMe.

kene molecules available for hydration and subsequent conversion to alcohol by loss of a proton.

Reaction of butan-1-ol with alkenes

A series of alkenes—some of which gave secondary carbonium ions on protonation and some which gave tertiary carbonium ions—were reacted with butan-1-ol in the presence of Al-clay at 95° and 150°C in sealed vessels. The alkenes used were: 2-methyl pent-1-ene, 2-methyl hept-1-ene, 4-methyl pent-1-ene, *cis* 4-methyl pent-2-ene, *trans* 4-methyl pent-2-ene, 3,3-dimethyl but-1-ene, hex-1-ene, and hex-2-ene. For all experiments, 0.5 g Al-clay (12% RH) was reacted with 6.25 mmole alkene, 6.25 mmole butan-1-ol, and 1.5 cm³ n-hexane solvents for 5 hr at 95° and 150°C.

The reactions catalyzed by the clay at 95°C gave rise to new products (t-ethers and t-alcohols) only in those reactions where the alkene was able to give a tertiary carbonium ion immediately upon protonation (Table 2). The alkenes which could give only primary or secondary carbonium ions on protonation did not yield new products.

At 150°C all of the alkenes studied reacted to give a range of products (Table 3), although the GLC trace was far cleaner than in those reactions catalyzed by concentrated acid. At this higher temperature some di-n-butyl ether was produced (Figure 2) from the butan-1-ol, as observed by Ballantine *et al.* (1981a, 1981b). In addition, each alkene reacted with butyl carbonium ions

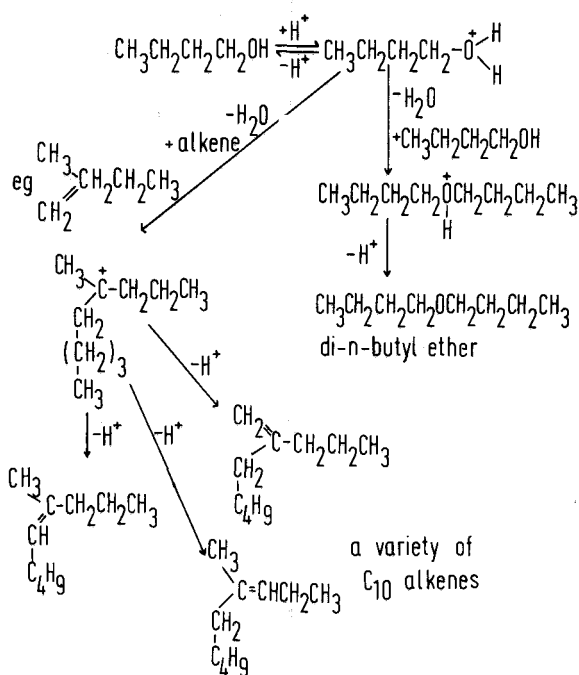


Figure 2. Diagrammatic representation of production and possible reaction pathways of butyl carbonium ions generated in the montmorillonite.

(produced by protonation and subsequent loss of water from the butanol) to give a C₁₀ carbonium ion which then lost a proton to give a C₁₀ alkene (Figure 2). The synthesis of di-(alk-1-yl) ethers from alcohols using a clay catalyst has been reported previously by Ballantine *et al.* (1981b), but in previous work involving the reaction of alkan-1-ols with hex-1-ene no mention was made of any ethers or alkenes arising from the reaction of the reactant alkene with a carbonium ion derived from the alcohol, the sole product of the reaction being 1-alkyl 2-hexyl ether and the 1-alkyl 3-hexyl ether (Ballantine *et al.*, 1981a).

In all experiments carried out in the present study at 150°C, the alkenes reacted with the butanol to give isomeric ether products. The reactions involving the methyl

Table 2. Summary of results for the reaction of various alkenes with butan-1-ol at 95°C in sealed vessels.¹

Alkene	t-ethers	Other ethers	Tertiary alcohols	Dimers of alkene	BuOH
2-methyl pent-1-ene	1.74	—	0.45	—	4.51
2-methyl hept-1-ene	1.40	—	0.32	—	4.85

Note that the following alkenes did not react under these conditions: 4-methyl pent-1-ene, *cis* 4-methyl pent-2-ene, *trans* 4-methyl pent-2-ene, 3,3-dimethyl but-1-ene, hex-1-ene, hex-2-ene. Values in millimoles.

¹ 0.5 g Al-clay (12% RH) + 6.25 mmole alkene + 6.25 mmole butan-1-ol + 1.5 cm³ n-hexane (5 hr, 95°C).

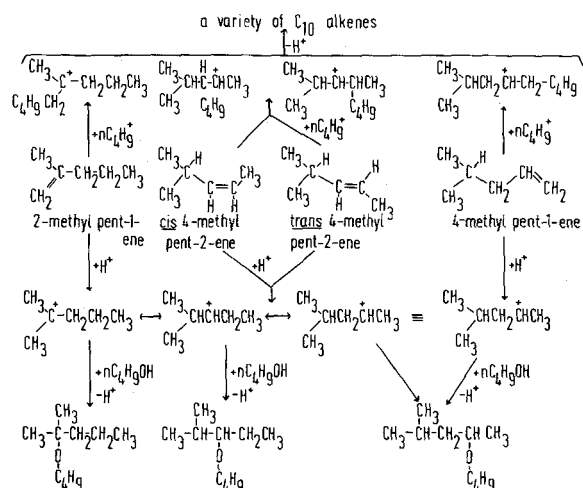


Figure 3. Diagram showing the various n -butyl ethers and C_{10} alkenes that can be derived from reactions involving the isomeric methyl pentenes and n -butanol.

pentenes give various amounts of 2-methyl 3-butoxypentane, 3-methyl 4-butoxypentane, and 2-methyl 2-butoxypentane (Figure 3) depending upon the position of protonation of the alkene in question and the

extent to which hydride shift occurred. The ratio of 2-methyl 4-butoxypentane to 2-methyl 3-butoxypentane could not be determined from GLC analysis because these compounds give unresolvable overlapping peaks. However, GLC-MS data indicated that the peak in question was the result of two ethers since molecular fragments having m/e 45 from the 4-butoxy ether and m/e 59 and 73 from the 3-butoxy ether were present.

As indicated in Table 3a, 2-methyl pent-1-ene gave predominantly the t -ether, 2-methyl 2-butoxypentane, whereas the remaining substituted pentenes gave mixtures of 2-methyl 3-butoxy and 2-methyl 4-butoxy ethers with minor amounts of 2-methyl 2-butoxypentane. It should be noted that on hydration 2-methyl pent-1-ene gave only 2-methyl pentan-2-ol, a t -alcohol, whereas the other methyl pentenes gave two secondary alcohols. 2-methyl hept-1-ene (Table 3b) behaved similarly to 2-methyl pent-1-ene except that there was slightly less C_{12} (compared with C_{10}) alkene produced by the reaction of a butyl carbonium ion with the 2-methyl hept-1-ene.

Of the two isomeric hexenes, hex-1-ene gave the greater yield of ether with the major product being the 1-butyl 2-hexyl ether (Table 3c). This ether was produced from the secondary carbonium ion formed di-

Table 3. Summary of results for the reaction of various alkenes with butan-1-ol at 150°C in sealed vessels.

(a) Alkene (methyl pentenes)	2-methyl 2-butoxy pentane	2-methyl 3-butoxy pentane and 2-methyl 4-butoxy pentane	C_{10} alkenes	2-methyl pentan-2-ol	Secondary alcohols	Di- n -butyl ether	Dimer of alkene	Butan-1-ol
	0.4	0.08	2.05	0.17	—	0.35	1.46	3.02
	0.11	1.5	0.12	—	0.07	0.25	—	4.02
	0.28	1.46	0.53	—	0.1	0.28	—	3.32
	0.18	0.74	0.41	—	0.1	0.32	—	4.28
(b) Alkene	2-methyl 2-butoxy heptane	Other ethers from BuOH + alkene	C_{12} alkene	2-methyl heptan-2-ol	Secondary alcohols	Di- n -butyl ether	Dimer of alkene	Butan-1-ol
	0.41	—	0.9	0.12	—	0.36	—	4.22
(c) Alkene	2-butoxy hexane	3-butoxy hexane	C_{10} alkenes	hexan-2-ol	Hexan-3-ol	Di- n -butyl ether	Dimer of alkene	Butan-1-ol
	2.33	0.46	0.04	0.06	0.02	0.34	—	2.74
	1.18	0.79	0.02	0.06	0.04	0.62	—	3.02
(d) Alkene	2,2-di-methyl 3-butoxy butane	2-methyl 2-butoxy 3-methyl butane	C_{10} alkene	2,3-di-methyl butan-2-ol	Secondary alcohols	Di- n -butyl ether	Dimer of alkene	Butan-1-ol
	0.17	0.19	0.04	0.08	—	0.23	—	5.39

0.5 g Al-clay (12% RH) + 6.25 mmole alkene + 6.25 mmole butan-1-ol + 1.5 cm^3 n -hexane (5 hr, 150°C). All quantities quoted are in mmoles of product.

rectly by protonation rather than the alternative carbonium ion which would be produced by a hydride shift and which would generate 1-butyl 3-hexyl ether. With hex-2-ene, relatively more 1-butyl 3-hexyl ether was produced because the carbonium ion required to give both the 2-hexyl and 3-hexyl ethers was generated directly from protonation of the alkene.

For 2,2-dimethyl but-1-ene the yield of all products was lower than with the remaining alkenes (Table 3). Two isomeric ethers were produced from the reaction with butan-1-ol, one of which is 2,2-dimethyl 3-butoxybutane formed by protonation of the double bond of the alkene followed by attack of the alcohol and loss of a proton. The secondary carbonium ion produced, however, undergoes a Wagner-Meerwein rearrangement (Fieser and Fieser, 1961) with migration of a methyl group to give a more stable carbonium ion $\text{CH}_3\text{-CH}(\text{CH}_3)^+\text{C}(\text{CH}_3)_2$. GLC/MS data indicated that this process did indeed occur to give 2,3-dimethyl 3-butoxybutane. Furthermore the alcohol produced in the reaction was that derived from the tertiary carbonium ion given by this Wagner-Meerwein rearrangement.

Reactions in the interlayer space

The reaction of alcohol and alkene molecules could, in principle, take place in solution, on the clay surface, or in the interlayer space of the clay catalyst. In control experiments made without clay catalyst, no reaction occurred. In a second set of experiments using AlCl_3 , together with the alcohol and alkene, none of the materials produced by the clay catalyzed reactions were found. The compounds 2-methyl pent-1-ene and *cis* 4-methyl pent-2-ene were also used for control experiments where they were stirred for 3 hr with equimolar amounts of butan-1-ol and concentrated sulfuric acid. GLC analysis of the organic reaction products indicated a low conversion of butanol together with a broad envelope of unresolvable peaks which consisted of alcohols, ethers, alkenes, and other polymerization and breakdown products of the alkene. It is apparent that the reactions must take place on the external surface of the clay particles, or in the interlayer space, or both.

The Al-clay equilibrated at 12% RH had a basal spacing of 15.4 Å. On immersion of this clay in 2-methyl pent-2-ene and hexan-1-ol the spacing increased to 15.9 Å and 17.9 Å, respectively. When the clay was immersed in a mixture of this alkene and alcohol, the spacing increased to 17.9 Å and remained there after heating to 95° and 150°C for 5 hr. Although both types of reactant molecules obviously had access to the interlayer space during the reaction, these data do not necessarily prove that reaction took place there.

A collapsed Al-clay was produced by heating at 500°C for 48 hr: reactions carried out using this material as a catalyst were compared with those using the normal, uncollapsed, clay (the reaction used was 2-methyl pent-1-ene + butan-1-ol). At 95°C, the normal clay gave

t-ether and t-alcohol products (Table 2), as did the collapsed clay, but the yield was only about 25% of that for the normal clay. At 150°C, the normal clay gave dimers of the reactant alkene and other ethers in addition to the t-ether and t-alcohol (Table 3a). The collapsed clay, however, gave a reduced yield of the t-ether and t-alcohol, but other products were not detected.

These results suggest that two types of sites may be involved in these reactions. First, a surface site may exist where carbonium ions can react with oxygenated species, such as the alcohol and water, but not with hydrocarbons. Second, the carbonium ions can react in the interlayer region with hydrocarbons to give dimers, etc. Moreover, these two sites would probably differ in acidity, with the interlayer site being more acidic. It is not completely clear whether the carbonium ions themselves can be formed on the surface and in the interlayer space, or only at one of these sites with subsequent migration to the reaction site.

DISCUSSION

The dramatic differences in the products formed by reactions at 95° and 150°C were probably due to loss of interlamellar water from the clay on heating at 150°C. As dehydration proceeds, the water remaining in the clay becomes more polarized by the Al cations and the proton donation ability is improved (Mortland, 1968). At 95°C protonation of the alkene took place only when a stable tertiary carbonium ion could be formed, whereas by 150°C the interlamellar water became sufficiently acidic to protonate alkenes that yielded less stable secondary carbonium ions and also sufficiently acidic to protonate butan-1-ol. This protonated alcohol subsequently lost water to yield the primary C_4H_9^+ carbonium ion which then reacted with other alcohol molecules (Ballantine *et al.*, 1981b) or reacted with alkenes to form larger alkene molecules.

If the reaction of the methyl pentenes with butan-1-ol is considered, 2-methyl pent-1-ene, which is the alkene that gives the most stable and easily produced carbonium ion, gave the lowest yield of ether but the largest yield of C_{10} alkene. The yield of ether was also significantly less at 150°C than at 95°C. At 150°C the extra high acidity in the clay enabled primary butyl carbonium ions to be formed; these ions easily attacked the nucleophilic double bond of an alkene. This process occurred as readily as protonation of the alkene, but the final step in the attack of the alkene by a butyl carbonium ion was the facile loss of a proton to form a C_{10} alkene. This loss took place more readily than the alternative attack of a butanol molecule on a protonated alkene regardless of any special orientation effects. At 95°C, however, because only 2-methyl pent-1-ene is protonated, the only possible reaction was that between butanol and 2-methyl pent-1-ene to produce the t-ether. As there were no other reactive species com-

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Резюме—Реакция 2-метил пент-2-ена с первичными спиртами (C_1 – C_{18}) при температуре 95°C в присутствии Al-монтмориллонита приводила к образованию 20–90% эфиров типа $R-O-C(CH_3)_2C_3H_7$. Меньшие количества производились при использовании вторичных спиртов, в то время как третичные спирты давали только следы этого эфира. Когда разные алкены реагировали с бутан-1-олем при 95°C в присутствии подобного катализатора, реакции не происходили до тех пор, пока алкен не был способен образовать третичного карбониевого иона немедленно после протонирования. В этом случае продуктом являлся третичный эфир $t-R-O-nC_4H_9$. Однако, при температуре реакции 150°C образовывались разные продукты, включая (1) эфир, полученный воздействием бутаноля на карбониевые ионы, произведенные либо непосредственно путем протонирования алкенов, либо путем сдвига гидрида из этого иона, (2) алкены, полученные воздействием ионов $n-C_4H_9^+$ (полученных путем протонирования и дегидратации бутаноля) на алкен, (3) ди-(бут-1-ил) эфир путем дегидратации бутаноля и (4) небольшие количества спирта путем гидратаций алкена. Различные значения реактивности ниже и выше 100°C связаны непосредственно с количеством воды, присутствующей в прослойках глины, и степенью кислотности. Хотя глина ведет себя как кислотный катализатор, реакции являются на много чище (более селективными), чем соответствующие реакции, катализируемые серной кислотой. [E.C.]

Resümee—Die Reaktion von 2-methyl-pent-2-en mit primären Alkoholen (C_1 – C_{18}) bei 95°C über einem Al-Montmorillonit ergab 20–90% Äther des Typs $R-O-C(CH_3)_2C_3H_7$. Geringere Ausbeuten wurden erreicht, wenn sekundäre Alkohole eingesetzt wurden. Tertiäre Alkohole ergaben nur Spuren dieses Äthers. Wenn unterschiedliche Alkene mit Butan-1-ol bei 95°C über einem ähnlichen Katalysator zur Reaktion gebracht wurden, trat keine Reaktion ein, außer das Alken war in der Lage, ein tertiäres Carbonium-Ion unmittelbar nach der Protonierung zu bilden. In diesem Fall war das Produkt ein tertiärer Äther $t-R-O-nC_4H_9$. Bei einer Reaktionstemperatur von 150°C wurde jedoch eine Vielzahl von Produkten gebildet einschließlich (1) Äther, unter der Einwirkung von Butanol auf die Carbonium-Ionen, entweder direkt bei der Protonierung von Alkenen oder durch Hydridverschiebung von diesen Ionen, (2) Alkene, unter der Einwirkung von $n-C_4H_9^+$ -Ionen (gebildet bei der Protonierung und Dehydrierung von Butanol) auf das Alken, (3) Di-(but-1-yl)-Äther, durch Dehydrierung von Butanol und (4) geringe Mengen von Alkohol, durch die Hydrierung von Alken. Die Unterschiede in der Reaktivität unter und über 100°C hängen direkt mit der Wassermenge zusammen, die in den Zwischenschichten des Tons vorhanden ist und mit der dort herrschenden Acidität. Obwohl der Ton als ein saurer Katalysator wirkt, sind die Reaktionen viel sauberer (selektiver) als vergleichbare Reaktionen, die durch Schwefelsäure katalysiert werden. [U.W.]

Résumé—La réaction de pent-2-ène méthyl-2 avec des alcools primaires (C_1 – C_{18}) à 95°C sur une montmorillonite-Al a fourni de 20–90% d'éthers du type $R-O-C(\text{CH}_3)_2C_3H_7$. Des rendements moindres étaient produits lorsque des alcools secondaires étaient employés, et des alcools tertiaires n'ont produit qu'une trace de cet éther. Lorsqu'on a fait réagir une variété d'alkènes avec du butan-1-ol à 95°C sur un catalyste similaire, aucune réaction ne se produisait à moins que l'alkène n'était capable de former un ion carbonium tertiaire dès que se passait la protonation. Dans ce cas, le produit était l'éther tertiaire $t-R-O-nC_4H_9$. A une température de réaction de 150°C cependant, une variété de produits ont été formés, comprenant (1) un éther par l'attaque du butanol sur les ions carbonium produits soit directement par la protonation des alkènes soit par déplacement hydride d'un tel ion, (2) des alkènes par l'attaque des ions $n-C_4H_9^+$ (dérivés de la protonation et la déshydratation du butanol) sur l'alkène, (3) l'éther di-but-1-yl) par la déshydratation du butanol, et (4) de petites quantités d'alcool par hydratation de l'alkène. Les différences de réactivité au dessus et dessous 100°C sont directement apparentées à la quantité d'eau présente dans l'espace interfeuillet de l'argile et au degré d'acidité trouvé là. Quoique l'argile se comporte comme un catalyste acide, les réactions sont beaucoup plus propres (plus sélectives) que des réactions comparables catalysées par un acide sulfurique. [D.J.]