7688 J. Org. Chem. 1993, 58, 7688-7693

Functional Selectivity in Friedel–Crafts Alkylations with Polyfunctional Reactants over Acid Zeolites

P. H. Espeel,* B. Janssens, and P. A. Jacobs

Centrum voor Oppervlaktechemie en Katalyse, K.U. Leuven, Kardinaal Mercierlaan, 92, B-3001 Heverlee, Belgium

Received July 8, 1993®

The selective formation of allyl-substituted aromatics over acid zeolites by electrophilic substitution of the aromatics with allyl alcohol is reported. In contrast to the reaction in homogeneous phase with H_2SO_4, this primary product is stable and almost no consecutive reactions of allyl-substitued aromatics are observed. When allyl chloride (7) is used as alkylating agent, nearly no allyl-substituted aromatic is obtained. HCl, liberated during reaction easily isomerizes the double bond, enabling a fast consecutive reaction. This implies that functional selectivity, which is unachievable in homogeneous phase can be easily reached over microporous solid Brönsted acids, provided no homogeneous acid is formed during reaction. The functional selectivity is attributed to the suppression of bimolecular side reactions and to the reduced isomerization rate of the double bond. For the electrophilic aromatic substitution, the turnover number of the acid site is about 120, confirming the true catalytic nature of this reaction. Deactivation of the catalyst is attributed to the oligomerization of an olefin, made upon hydride transfer to an allyl cation.

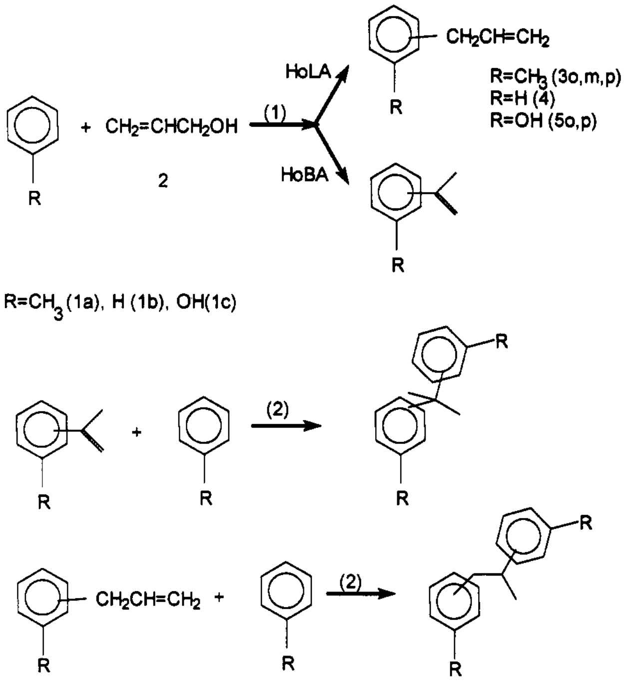
Introduction

The Friedel–Crafts reaction has been recognized as a very versatile tool for substituting aromatic rings.[1] However, the latter reactions are almost limited to the substitution of aromatic substrates with monofunctional reagents. Indeed, when more than one reactive function is present in the reagent, the reaction occurs with an almost total absence of "functional" selectivity and usually does not end before all reactive functions in the substrate are consumed. The alkylation of toluene (**1a**) or phenol (**1c**) with allyl alcohol (**2**) is a typical example. With a homogeneous Brönsted acid, an isopropenyl aromatic was claimed to be the primary electrophilic aromatic substitution (EAS) product, while with a Lewis acid allyltoluene was the primary product. However, after formation of an allyl- or isopropenyl-substituted aromatic the reaction further proceeds with the formation of diaryl-substituted propanes[2] as shown in Scheme I.

Functional selectivity in reactions with polyfunctional reagents can only be achieved if the functional groups show pronounced differences in reactivity. Typical examples are the reaction of halogen-substituted aroyl chlorides[3] and unsaturated carboxylic acids[4] for which the most reactive functions are the aroyl and the double bond, respectively. It is clear that functional selectivity could lead to shortened ways to synthesize valuable fine chemicals and increase considerably the applicability of Friedel–Crafts methods.

The main reason for the absence of functional selectivity in traditional Friedel–Crafts reactions is related to the high activity of the acids used, thus failing to discriminate among different functional groups. The application of less-reactive acids is obvious.

Scheme I. Primary (1) and Consecutive (2) EAS Reactions with Allyl Alcohol over Homogeneous Lewis (H_oLA) or Brönsted Acids (H_oBA).



Zeolites in their acidic form are moderately active in Friedel–Crafts alkylations compared to homogeneous Lewis and Brönsted acids.[5] Therefore they seem potential candidates for exhibiting functional selectivity in Friedel–Crafts reactions. The possible occurrence of selective adsorption of a multifunctional reagent in the zeolite pores and the inhibition of consecutive transformations of primary products by steric constraints of the pore structure further support this hypothesis.

In the present study the possibility to achieve functional selectivity in EAS reactions was investigated using the allylation of toluene, benzene, and anisole in mineral acid medium and in microporous solid acids. The reaction of toluene and allyl alcohol is chosen as a model test.

® Abstract published in *Advance ACS Abstracts*, December 1, 1993.

[1] Olah, G. *Friedel–Crafts Chemistry*; John Wiley & Sons: New York, 1974; p 421.

[2] Olah, G. *Friedel–Crafts Chemistry*; John Wiley & Sons: New York, 1974; p 419.

[3] Hart, R. T.; Teble, R. F. *J. Am. Chem. Soc.* **1950**, *82*, 3286.

[4] Thomas, C. A. *Anhydrous Aluminium Chloride in Organic Chemistry*; Reinhold Publ. Co., 1941; p 486.

[5] Venuto, P. B.; Hamilton, L. A.; Landis, P. S.; Wise, J. J. *J. Catal.* **1966**, *4*, 81.

0022-3263/93/1958-7688$04.00/0

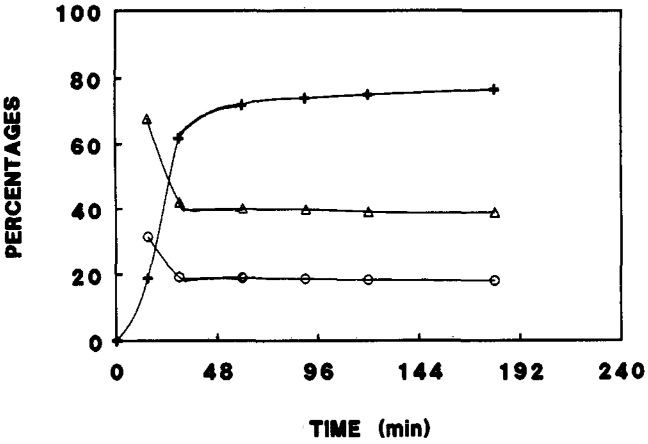


Figure 1. Conversion in time of **2** (+) and selectivity to **3o,m,p** (△) and **6** (○) in time for the reaction of **2** with **1a** over HUSY26 under standard conditions.

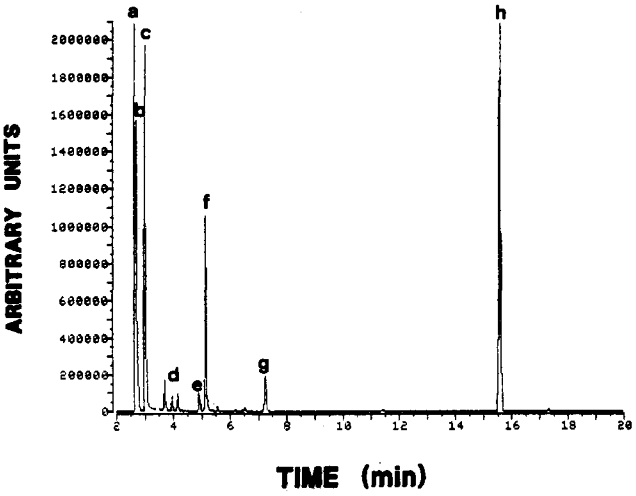


Figure 2. Total ionization chromatogram of the vapor phase for the reaction of **1a** over HUSY26 with **2** under standard conditions: (a) N_2, (b) ethene, (c) propene, (d) (3) butene isomers, (e) propenal, (f) propanal, (g) allyl alcohol, (h) toluene.

Results

The reaction of toluene (**1a**) with allyl alcohol (**2**), performed in standard conditions in presence of ultrastable Y zeolite (HUSY26), yields mainly the three allyltoluene isomers (**3o,m,p**) together with considerable amounts of 3,3′-oxybis(1-propene) (**6**). In Figure 1 conversion of **2** and selectivities in time to **3o,m,p** and **6** are given. The total selectivity for these two products is 65%. From GC and HPLC analysis was found that the amount of secondary reaction products (diallylation of toluene and consecutive reaction of the allyl double bond) was negligible. The remaining part of the mass balance is made up by gaseous products. A total ionization chromatogram obtained by GC-MS analysis of the vapor phase is shown in Figure 2. The main components are ethene, propene, and propanal and only minor amounts of the butene isomers and propenal are found. In Table II a typical product distribution is given. As can be seen in Figure 1 the catalyst is deactivated in time. Nevertheless, the turnover number, i.e. the number of times each proton of the zeolite catalyzes the formation of allyltoluene is about 120, which indicates that the reaction is truly catalytic.

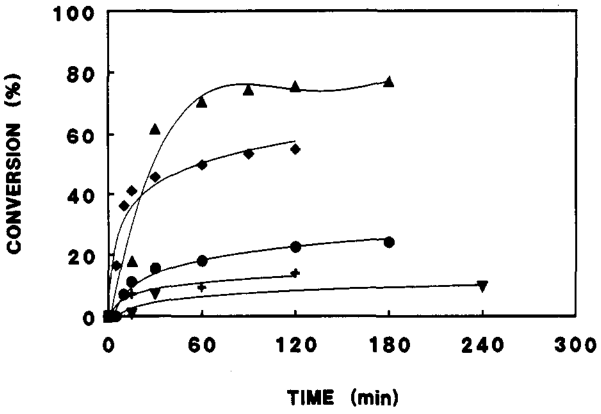


Figure 3. Conversion of **2** in the reaction with **1a** under standard conditions over (▲) HUSY26, (●) HMOR100, (▼) SIAL4, (♦) HBETA16, and (+) K10.

Table I. Notation, Origin, Overall, and Framework Composition and Particle Size of the Different Catalyst Samples

		composition on oxide basis (wt %)				
notation	origin	SiO_2	Al_2O_3	Na_2O	particle size (μm)	framework Si/Al
Y-zeolites						
HUSY03	Zeocat	73.92	23.27	2.81	3.2	2.7
HUSY12	*a*	75.10	23.60	1.30	3.2	12.0
HUSY19	*a*	90.79	9.08	0.13	3.2	19.0
HUSY26	*a*	92.39	7.50	0.11	3.2	26.0
HUSY90	*a*	95.87	4.07	0.06	3.2	90.0
Mordenite						
HMOR100	*a*	99.15	0.84	0.005	29	100
Beta						
HBETA16	P&Q	93.65	6.35	0.10	1-2	16.0
silica-alumina						
SIAL4	Grace	82.5	17.5	0.0		4.0

[a] Same as above.

Table II. Product Selectivities in the Reaction of 2 with 1a (at 40% conversion of 2) over HUSY26 under Standard Conditions

product	product selectivity
3o,m,p	43
3,3′-oxybis(1-propene)	21
diallyltoluene	<1
1,2 ditolylpropane	<1
ethene	10
propene	13
butenes	2
propenal	1
propanal	5
sum	95

The absence of consecutive reactions of **3o,m,p** was verified by contacting under standard conditions allylbenzene (**4**) with **2** on one hand and with toluene on the other hand. The conversion of **4** in each case was very low, implying that under the considered conditions **3o,m,p** is stable. Thus the hydroxyl function reacts without interference of the double bond.

The performance of HUSY26 has been compared with other catalysts. In Figure 3 the conversion of **2** in time is represented. Zeolites with a tridimensional pore structure, such as HUSY26 and HBETA16, show acceptable conversion. Zeolites with a monodimensional pore structure, such as HMOR100, show an activity comparable to the amorphous silica alumina and K10, an acid-treated montmorillonite. The selectivity to **3o,m,p** is given in Figure 4. The isomer distribution in the **3o,m,p** fraction at 60% conversion is given in Table III. The performance of the different solid acids can be compared with concentrated H_2SO_4. On acids where no steric constraints

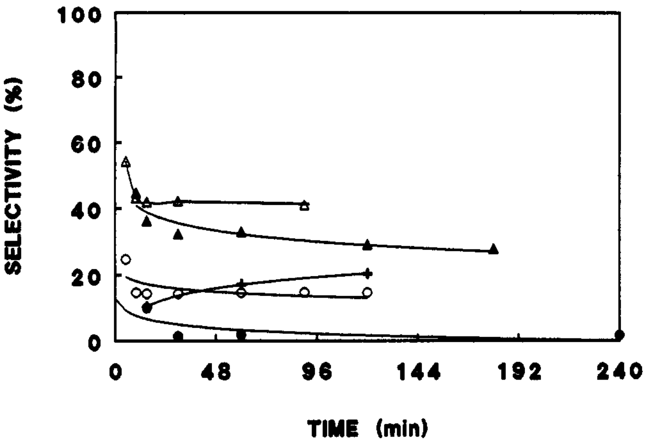


Figure 4. Selectivity to **3o,m,p** in the reaction of **2** with **1a** under standard conditions over (▲) HMOR100, (△) HUSY26, (○) HBETA16, (+) K10, and (●) SIAL4.

Table III. Isomer Distribution in the 3o,m,p Fraction Obtained over Different Catalysts at 60% Conversion

catalyst	isomer distribution ortho	meta	para
HUSY26	53	14	33
HBETA16	45	14	41
HMOR100	44	10	46
K10	51	15	34
H_2SO_4	51	16	33

Table IV. Product Selectivity at a Given Conversion Level (%C) in the Reaction of 2 with 1a at Different Temperatures with 10 wt % Catalyst and an Aromatic/Alkylating Agent Ratio of 10. The Selectivity to "Others" Corresponds with the Selectivity toward Gaseous Products and the Products Not Removed from the Catalyst

T (K)	%C	% 3o,m,p	% 6	% others
373	10	33	42	25
393	20	36	35	29
423	40	43	21	36
453	43	46	18	36

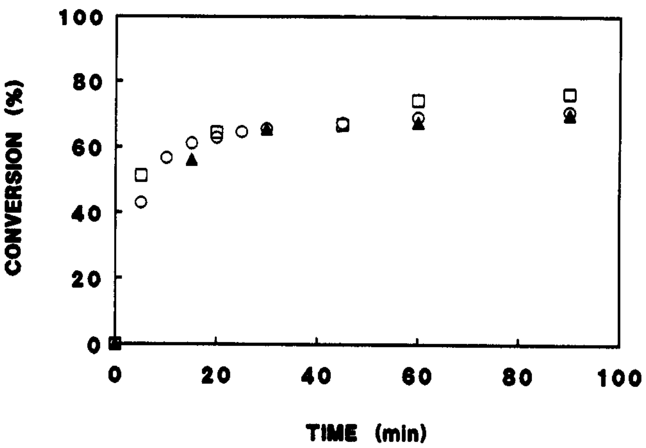


Figure 5. Conversion of **2** in the reaction with **1a** at 423 K, 10 wt % catalyst, and with a **1a**/**2** molar ratio of (▲) 5, (○) 10, and (□) 20.

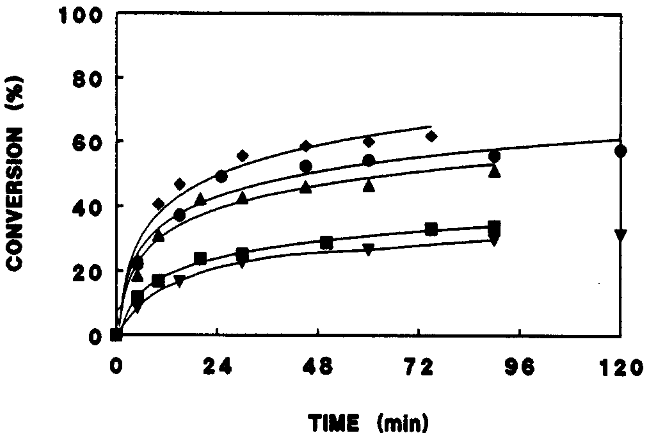


Figure 6. Conversion of **2** in the reaction with **1a** under standard conditions over acid faujasites with (■) 6.5, (▲) 1.8, (●) 1.2, (♦) 0.9, and (▼) 0.3 Al atoms per super cage on average.

Table V. Product Selectivities in the Reaction of 2 with 1a at 423 K, 10 wt % Catalyst, and with Varying Aromatic/Alkylating Agent Ratio (AR/AA). The Data are Given at 60% Conversion of the Alkylating Agent

AR/AA	% 3o,m,p	% 6	% others
5	26	19	55
10	43	21	37
20	50	6	43

are to be expected (HUSY26, K10, H_2SO_4) the isomer distribution is virtually identical. On acids with decreasing pore size (HUSY26 > HBETA16 > HMOR100), para-selectivity increases.

Reaction of **1a** with **2** in the presence of 96% H_2SO_4 at room temperature showed that the primary product is **3o,m,p** and not isopropenyltoluene as claimed in earlier work.[1] This was unambiguously demonstrated with ^{1}H-NMR spectroscopy. However, the yield of **3o,m,p** was low as a result of consecutive reactions such as tar formation.

One of the main side reactions is the formation of 3, 3′-oxybis(1-propene) (**6**). This reaction is bimolecular in **2** and unfavored at higher temperatures (Table IV). Therefore for optimization purposes, yields in **3o,m,p** were determined at various reaction temperatures and molar ratios of aromatic to alkylating agent.

From the temperature dependence of the initial rate of **3o,m,p** formation, an apparent activation energy of 97 kJ/mol is calculated. Interestingly, while the yield in **6** decreases with temperature the formation of **3o,m,p** and gaseous products is increased (Table IV).

In Figure 5 the conversion of **2** in time is represented for varying aromatic/alkylating agent ratios at constant catalyst percentage. It is clearly seen that the final conversion level is independent of the aromatic/alkylating agent ratio. The corresponding selectivities are given in Table V. The use of higher ratios results in an increased selectivity for **3,o,m,p** at the expense of **6**. At low ratios, high selectivities for gaseous byproduct are seen.

The influence of the Al content of the faujasite structure and consequently of the acid site density and acid strength on conversion and **3o,m,p** selectivity is given in Figures 6 and 7, respectively. The optimal Si/Al ratio is 26 which on average corresponds with one acid site per supercage. The EAS selectivity is only catalyst dependent and hardly changes with conversion. The dependence of product selectivity at a given conversion on the Al content is given in Table VI. The sample with an optimum site-density, as far as conversion and EAS selectivity is concerned, also shows the best selectivity for monoalkylated products (**3o,m,p**) and the lowest selectivity for side products (% others). The bimolecular ether formation (% of **6**) is not dependent on site-density.

Since allyl chloride (**7**) is a much less-expensive source of allyl cations, it is important to know whether reaction

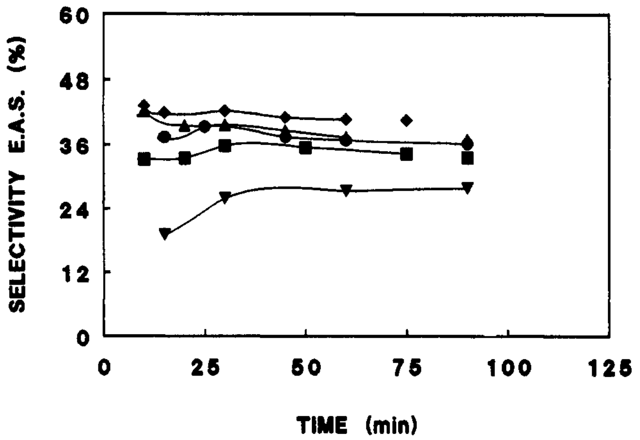


Figure 7. Selectivity to EAS products in the reaction of **1a** allylation under standard conditions over acid faujasites with (■) 6.5, (▲) 1.8, (●) 1.2, (♦) 0.9, and (▼) 0.3 Al atoms per supercage on average.

Table VI. Product Selectivities in the Reaction of 1a with 2 over Faujasite-Type Catalysts with Varying Al Content

Al/supercage	% C	% **3o,m,p**	% **6**	% others
6.5	28	32	16	51
1.8	18	47	29	25
1.2	22	48	25	27
0.9	23	54	26	20
0.3	23	26	20	54

of **1a** with **7** would also lead to the selective formation of **3o,m,p**. Performed under standard conditions, the main products are 1,1-ditolylpropane and 1,2-ditolylpropane. Only minor amounts of **3o,m,p** are isolated. GC-MS indicates the formation of 1-(*o,m,p*-tolyl)-2-chloropropane in minor quantities. Performed in an open vessel, which allows removal of HCl, the selectivity for **3o,m,p** is very much enhanced.

Finally reaction between 3-buten-1-ol and **1a** under standard conditions gives 3-tolyl-1-butene as the main product. The conversion is very low, although the molar ratios and amount of catalyst are the same as for reaction of **2** with **1a**.

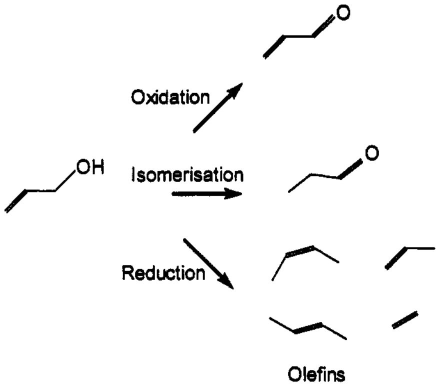
The allyl substitution is not limited to reaction with **1a**. For reaction of benzene (**1b**) and anisole (**1d**) with **2**, the allyl-substitued aromatic was the sole EAS product.

Discussion

Reaction Selectivity in the Allylation of Toluene with Allyl Alcohol. In literature it was reported that in the presence of $AlCl_3$ the primary reaction product of **1a–c** with **2** is an allyl aromatic,[6,7] while in the presence of a protonic acid (H_2SO_4, H_3PO_4) an aralkyl alcohol is formed which dehydrates toward an isopropenyl aromatic.[8] The yield of the latter product is low as a result of secondary reaction of the double bond. No fundamental reason was advanced for the different behavior of Lewis and Brönsted acids.

We, however, do find and verify with ^{1}H-NMR and mass spectrometry and comparison with the spectra of authentic samples that in the presence of 96% H_2SO_4 the primary product of **1a** with **2** at room temperature is an allyl-substituted aromatic rather than an isopropenyl aromatic. Its yield is rather low due to consecutive reactions. This implies that under the conditions tested no functional selectivity in the homogeneous phase can be reached, using Brönsted or Lewis acids.

Scheme II. Byproduct Formation From 2 with a Solid Brönsted Acid as Catalyst.



The primary EAS product for the reaction over solid Brönsted acids is always an allyl aromatic, which is stable under the conditions tested, since nearly no consecutive reactions, i.e. dialkylation or reaction of the allylic double bond was observed. Besides EAS products, an important fraction of diallyl ether (**6**) is formed. The latter selectivity increases as expected with decreasing temperature and decreasing aromatic/alkylating agent ratio. Optimal conditions for the combined formation of **3o,m,p** and **6** can also be selected (a ratio **1a**/**2** of 10 and a temperature of 423 K).

Byproducts, which represent about 35% of converted **2**, can be considered as originating either from reduction, isomerization, or oxidation of **2** as represented in Scheme II. Ethene, propene, and the butene isomers are reduction products, while propanal and propenal are the outcome of isomerization and oxidation, respectively. Mechanistically, propene is formed upon hydride transfer to an allyl cation. Its dimerization provides hexenes, which can crack into ethene and butenes. Considering Table II, it is undeniable that the oxidoreduction balance is out of equilibrium as reduction reactions strongly dominate. Recently, Hutchings et al. studied the conversion of **2** over acid zeolites at temperatures between 523 and 623 K.[9,10] Apart from the similarity in products formed, a close inspection of their results reveals the same imbalance in the ratio of oxidation over reduction reactions, which remained unnoticed by the authors. This imbalance suggests the presence of an "hidden" source of hydride. The only possible source of hydride results from oligomerization of propene and is intrinsically an autocatalytic reaction. Oligomerization of propene and hydride transfer is at the same time the main source of catalyst deactivation, which implies that toluene does not interfere in the deactivation mechanism. Indeed, as shown in Figure 5, the conversion level of **2** is independent of the molar ratio **1a**/**2** and only determined by the weight percentage of catalyst versus alkylating agent implying that consecutive reactions of primary EAS products are not responsible for catalyst deactivation.

---

(6) Huston, T. C.; Sager, D. D. *J. Am. Chem. Soc.* **1926**, *48*, 1955.

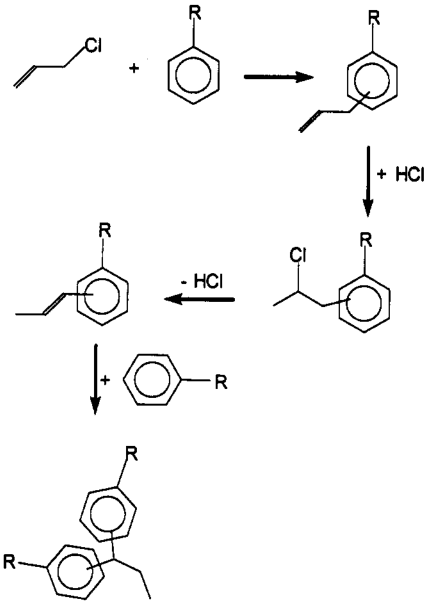
(7) Olah, G. *Friedel–Crafts Chemistry*; John Wiley & Sons: New York, 1974; p 442.

(8) Losev, I. P.; Smirnova, O. V.; Ryadneva. Chem. Abstr. **1955**, *49*, 832.

(9) Hutching G. J.; Lee, D. F.; Williams, C. D. *Stud. Surf. Sci. Catal.* **1991**, *69*, 389.

(10) Hutchings, G. J.; Lee, D. F.; Williams, C. D.; *J. Chem. Soc. Chem. Commun.* **1990**, 1474.

Scheme III. Reaction Mechanism in the Allylation of Alkyl Aromatics with Allyl Chloride over Solid Microporous Brönsted Acids.



Allylation with 3-Buten-1-ol or Allyl Chloride. The reasonably high activity of zeolites in the allyl substitution on aromatics accompanied with high functional selectivity is closely related to the nature of **2**. In reaction of toluene with 3-buten-1-ol, the double bond of this molecule is activated rather the hydroxyl function. This leads to the formation of 1-hydroxy-3-tolylbutane which is partly dehydrated to 3-tolyl-1-butene, but with an extremely low yield. This implies that **2** is a very specific allylating agent as the olefinic double bond activates the hydroxyl group of an unsaturated primary aliphatic alcohol. Consecutive reaction of **3o,m,p** is suppressed by steric constraints imposed by the pore architecture of the microporous environment. A similar activity enhancement of the Cl-function in **7** should occur, leading also to the selective formation of **3o,m,p** in reaction with toluene. However, only a very low yield of **3o,m,p** was found. Based on the product selectivity, the reaction mechanism represented in Scheme III is proposed. As for **2**, the primary EAS product is **3o,m,p**. However in the presence of HCl, this α-olefin is isomerized to a β-olefin, which has an activated double bond in direct conjugation with the aromatic ring. Finally, this reactive molecule is converted to 1,1-ditolylpropane. This reaction sequence is supported by the presence of 1-tolyl-2-chloropropane. Comparison of the reaction products for **2** and **7** stresses that the "homogeneous" acid is responsible for the double bond isomerization rather than the solid acid.

Zeolite Specificity in Friedel–Crafts Catalysis. One of the main recognized advantages of zeolite-catalyzed Friedel–Crafts chemistry, is the ability to favor the formation of the smallest positional isomer.[11] As shown in Table IV, in the present reaction only a moderate increase of 12% in para isomer selectivity is achieved when performing the reaction over the solid Brönsted acid with the smaller pores (HMOR100). This is reasonable given the low steric constraints imposed by the pore structure on the small substituting allyl cation. However, pore structure imposes a significant restriction on the consecutive reactions of **3o,m,p**. This, together with the reduced double bond isomerization is the basis for the functional selectivity in this reaction.

The allyl substitution of **1a** is acid-catalyzed as Brönsted sites are used more than 100 times. The optimal Si/Al ratio (26) corresponds to a specific site density of one Brönsted acid site per supercage. At higher acid site density, the aromatic substrate which is an H-bond acceptor may be deactivated. With such catalysts, side reactions of bimolecular nature and giving rise to gaseous byproducts and catalyst deactivation become increasingly important. Differences in acid strength can be excluded as the selectivity-determining parameter as the Brönsted sites are already isolated and identical in strength from a concentration of 3–4 per supercage.[12]

Conclusion

The allylation of aromatics with allyl alcohol is possible with good selectivity over acid zeolites as catalysts and yields allyl-substituted aromatics as EAS products. Such functional selectivity is unachievable in a reaction catalyzed by homogeneous Brönsted acids or in a reaction in which a homogeneous Brönsted acid is liberated as the primary product easily undergoing consecutive reaction in its presence.

Steric restriction imposed by the pore structure, suppressing consecutive reactions of the allyl aromatics and the reduced double bond isomerization, are the two most important reasons for this functional selectivity. This reaction clearly demonstrates the unique properties of solid acids. In this way microporous solid Brönsted acids could considerably broaden the scope of and give a new impetus to Friedel–Crafts catalysis in many fields of organic chemistry.

Experimental Section

General Procedure of Allylation of Aromatics with Allyl Alcohol. The reactions were performed in a high pressure stirred batch reactor of 300 mL. The conditions were, except when otherwise stated, a reaction temperature of 423 K, 1 mol of aromatic, 0.1 mol of alkylating agent (**2**), and 0.05 mol of internal standard (cyclohexane). The reactor was filled with the aromatic and catalyst and then heated to reaction temperature. In order to have a neat starting point of the reaction, the alkylating agent, together with an internal standard (cyclohexane) was injected at reaction temperature in a catalyst–aromatic suspension. The conversion of the reactant and product yields were determined based on the internal standard. After reaction, the reactor was cooled down to room temperature and the solution was filtered. Different purification steps were used to isolate the products. In all cases, selectivities are compared at similar substrate conversion.

The Overall Compositions of the Different Catalysts were determined by standard chemical methods and are given in Table I. All catalysts were obtained from the respective suppliers in the acid form with the exception of HUSY03 which was obtained in the Na^+ form. The latter sample was ion-exchanged in reflux conditions in an excess of a 0.5 N aqueous ammonium chloride solution. Afterwards the sample was washed with distilled water till chloride free and dried at 333 K. The framework composition of the zeolites was determined with ^{29}Si MAS NMR (Bruker MSL400) at a frequency of 79.5 MHz and a spinning rate of 12.5 kHz according to reference.[13] All materials were activated under

---

[11] I. E. Maxwell, I. E.; Stnk, W. H. J. *Stud Surf. Sci. Catal.* **1991**, *58*, 571.

[12] Dwyer, J.; Dewing, J.; Karim, K.; Homes, S.; Ojo, A. F.; Garforth, A. A.; Rowlence, D. J. *Stud. Surf. Sci. Catal.* **1991**, *69*, 1 and refs therein.

[13] Engelhardt G.; Lohse, U.; Lippmaa, E.; Tarmak, M.; Mägi *Z. Anorg. Allg. Chem.* **1981**, *482*, 49.

a stream of oxygen while heating at a rate of 2 K/min up to 723 K. Afterwards the catalysts were cooled down to room temperature under oxygen atmosphere and rapidly added to the aromatic to avoid moisture uptake.

The products, both the composition of the liquid phase and of the gas phase in thermal equilibrium, were analyzed by gas chromatography. Structural identification of the products, after separation was done with GC-mass spectrometry (HP 5988A) and ^{1}H-NMR spectroscopy (Brücker AX 300). Chemical shifts are reported relative to TMS. The GC was equipped with a CP-sil-5-CB column (Chrompack) of the WCOT-type of 25-m length.

Allylation of Benzene. Following the general procedure, reaction of **1b** with **2** over HUSY26 gave **4** with a yield of 45%. After reaction and filtration of the solution, benzene was distilled off. The residue was purified by chromatography on a reversed-phase column (acetonitrile, water): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.10 (m, 5H), 5.86 (m, 1H), 5.01 (1H), 4.97 (1H), 3.24 (d, J = 6.7Hz, 2H); MS, *m/e* 118 (M^+, 69), 117 ($M^+ - H$, 100), 91 ($M^+ - C_2H_3$, 38), 78 (M^+ – allyl, 34).

Allylation of 1a. In the reaction of **1a** with **2** under conditions specified in the result section a mixture of three isomers was obtained. After filtration, the **3o,m,p** was distilled and purified by high pressure preparative liquid chromatography on a reversed-phase column RP C18 of Waters (acetonitrile, water). The ^{1}H-NMR spectrum of the three isomers undoubtedly confirmed the presence of the allyltoluene isomers: δ = 7.14–7.05 (4H), 5.96 (1H), 5.19–5.01 (2H), 3.37–3.33 (2H), 2.32–2.25 (3H). The isomer distribution was determined by comparison of the retention times of the three isomers, synthesized according to an established Grignard procedure,[14] with the product mixture.

Allylation of 1d. The reaction of anisole with **2** under standard conditions over HUSY26 yields 37% EAS products. The yield of 2-allylanisole was 20%:MS, *m/e*, 148 (M^+, 100), 147 ($M^+ - H$, 20, 133 ($M^+ - CH_3$, 20), 117 ($M^+ - CH_3O$, 40), 91 (tropylium ion, 57), 77 (phenyl ion, 89), ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 6.9 (m, 4H), 5.9 (m, 1H), 5.0 (m, 2H), 3.8 (s, 3H), 3.4 (d, J = 6 Hz, 2H). The yield of 4-allylanisole was 17%:MS, *m/e*, 148 (M^+, 100), 147 ($M^+ - H$, 48, 133 ($M^+ - CH_3$, 36), 121 ($M^+ - C_2H_3$, 71), 117 ($M^+ - CH_3O$, 70), 91 (tropylium ion, 48), 77 (phenyl ion, 20); ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 6.9 (d of d, 4H), 5.9 (m, 1H), 5.0 (m, 2H), 3.71 (s, 3H), 3.3 (d, J = 6 Hz, 2H).

Identification of 6. During reaction of **1a,b,c** and **2**, **6** was formed with a yield of 20%. The mass spectrum gives convincing evidence for its nature: MS, *m/e*, 84 (M^+ ,5), 83 ($M^+ - H$, 11), 41 (C_3H_5, 100).

1,1-Ditolylpropane: MS, *m/e*, 224 (M^+, 13), 195 (M^+ – Et, 100).

1,2-Ditolylpropane: MS, *m/e*, 224 (M^+, 8), 119 (M^+ – 1 – tolylmethyl, 100).

The following product was present in minor amounts and has only been identified with GC-MS. **2-Chloro-1-tolylpropane:** MS, *m/e*, 168 (M^+, 12), 170 ($M^+ + 2$, 4), 133 ($M^+ - Cl$, 5), 105 ($M^+ - C_2H_4Cl$, 100), 91 (tropyliumion, 12).

Registry No. Allyl alcohol, 107-18-6; allyl chloride, 107-05-1; toluene, 108-88-3; anisole, 100-66-3; benzene, 71-43-2; diallyl ether 557-40-4; allylbenzene, 300-57-2; **3o**, 1587-04-8; **3m**, 3333-20-8; **3p**, 3333-13-9; *o*-allylanisole, 3698-28-0; *p*-allylanisole, 140-67-0; 1,1-ditolylpropane, 52991-27-2; 1-tolyl-2-chloropropane, 10304-81-1.

Acknowledgment. P. H. Espeel and B. Janssens acknowledge the Flemish National Science Foundation (N.F.W.O) and I.W.O.N.L., respectively, for a grant as research assistant. The authors appreciate financial assistance from N.F.W.O. and from the Belgian government in the frame of a IUAP-PAI project. In this respect, the paper does not intend to express official views.

---

(14) Bragole, R. A. Ph. D. Dissertation, Yale University, May 1965.