Mechanistic Investigations of Liquid-phase Direct Alkylation of Benzene with \( n \)-Heptane Using Proton-exchanged Montmorillonite Catalysts

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The direct alkylation of benzene with \( n \)-heptane was investigated using noble-metal-free montmorillonite as a solid acid catalyst. It was found that the catalytic activity of proton-exchanged montmorillonite increased after pretreatments such as heating and ultrasonic irradiation. Aluminum-exchanged montmorillonite was also found to be a good catalyst. Moreover, during the reaction using proton-exchanged montmorillonite, the product selectivity depended on the interlayer distance of the catalyst. Detailed time-course analysis of the selectivity of the alkylation product revealed that, in the case of the catalysts with smaller interlayer distances, the bimolecular reaction occurred preferentially at the surface, resulting in higher selectivity with respect to the target C7 alkylated products (Ph-C7). On the other hand, the monomolecular cracking of heptane in the interlayer spaces resulted in a stable \( t \)-butyl cation, yielding \( t \)-butylbenzene. Monomolecular cracking also occurred when H-ZSM-5 was used as the catalyst, and the main product was isopropylbenzene.

Keywords
Montmorillonite, Solid acid catalyst, Alkylation, Benzene, Heptane

1. Introduction

The direct conversion of alkanes into raw materials for chemical products is important as it can result in lower costs and fewer synthesis steps as compared with the case for conventional processes, which use halogenated alkanes\(^{1)\}~^{3)}\). On the other hand, alkanes are composed only of C–C and C–H single bonds and therefore have low reactivity. Hence, they are mostly used as fuels after industrial cracking, isomerization, and steam reforming\(^{4)}\). Many researchers have been working on catalysts suitable for the direct conversion of alkanes\(^{5)}~^{11)}\). For example, selective alkane conversion reactions, such as partial oxidation to alcohol or aldehydes\(^{6)}~^{8)}\) and dehydrogenation to alkenes\(^{9)}~^{11)}\), have been reported. In this study, we focused on the direct alkylation of benzene using alkanes. The alkylation of benzene with ethane or propane at 300 °C or higher using Pt and Pd/H-ZSM-5 has been reported\(^{12)}~^{18)}\). There have also been reports on its alkylation with alkanes with relatively longer carbon chains, such as hexane, using Pt/H-ZSM-5 and PtGa/H-ZSM-5\(^{19)}~^{20)}\). In addition, a few noble-metal-free catalysts such as H-ZSM-5 have also been reported. However, the selectivity of these catalysts with respect to alkylated benzenes is low\(^{19)}~^{20)}\). Only HF-SbF\(_5\), which is a homogeneous super strong acid, yields a product with high selectivity at room temperature\(^{21)}\). On the other hand, there has been no report on the synthesis of products with high selectivity using a noble-metal-free heterogeneous catalyst.

Montmorillonite is a cation-exchangeable clay compound with a layered structure. The ion-exchange ability of its interlayer spaces allows for the design and synthesis of several types of Bronsted and Lewis acid catalysts\(^{22)}~^{28)}\). For example, Onaka and coworkers reported Sn-exchanged montmorillonite catalysts for liquid-phase organic synthesis through nucleophilic addition reactions\(^{29)}~^{32)}\). Sun and coworkers developed Nb-montmorillonite for the synthesis of 5-hydroxymethylfurfural from glucose\(^{33)}\). Moreover, proton- and aluminum-exchanged montmorillonites have been employed as solid acid catalysts for many carbon-carbon/
heteroatom bond-forming reactions such as the carbosilylation of olefins\(^{34}\)~\(^{36}\). In addition, we had reported previously that aluminum-exchanged montmorillonite (Al-mont) shows good catalytic performance during the direct alkylation of benzene with heptane for the formation of alkylated products with a carbon chain of 7 carbon atoms (Ph-C\(_7\)) at 150 °C\(^{37}\). Proton-exchanged montmorillonite (H-mont) has also been found to be a good catalyst for the selective alkylation of benzene\(^{37}\). In this study, the relationship between the interlayer distance and product selectivity of montmorillonite as a catalyst was elucidated using H-mont catalysts that exhibited different interlayer distances through pretreatments.

2. Experimental

2.1. General Method

Shimadzu ICPS-8100 was used to perform inductively coupled plasma (ICP) emission spectroscopy for quantitative elemental analysis. The powder X-ray diffraction (XRD) patterns of the various catalysts were recorded at room temperature using Rigaku Ultima IV system with Cu-K\(\alpha\) radiation source. Analytical gas chromatography with flame-ionization detection (GC-FID) was performed using Shimadzu GC-2025 with DB-1 columns. Further, analytical GC-mass spectrometry (MS) was performed with Shimadzu GC-2020 Plus system with QP2010SE and DB-1 columns.

2.2. Material

Unless otherwise noted, all materials were purchased from Kanto Chemical Co., Inc., FUJIFILM Wako Pure Chemical Corp., Tokyo Chemical Industry Co., Ltd. and Sigma-Aldrich Co. LLC. Sodium-exchanged montmorillonite (Na-mont; Na\(_{0.33}\)O\(_{1.33}\)Si\(_8\)Al\(_{3.34}\)Mg\(_{0.66}\)Fe\(_{0.19}\)O\(_{20}\)) was purchased from Kunimine Industry Co., Ltd., Japan as Kunipia F. Finally, HSZ-820 (Si/Al = 23.2, Tosoh Corp.) was used as H-ZSM-5.

2.3. Catalyst Preparation

The cation-exchanged montmorillonite catalysts were prepared by the ion-exchange method. Proton-exchanged montmorillonite (H-mont) was prepared via the cation-exchange method from Na-mont (3.0 g) using 200 mL of aqueous HCl (1.1 wt%) solution. The mixture was stirred at 90 °C for 24 h, and the obtained slurry was filtered and washed with 1 L of distilled water to ensure the removal of chlorine. This was followed by drying at 110 °C in air to afford Al-mont as a white-gray powder.

2.4. Catalytic Reaction

The reaction between n-heptane and benzene was performed as follows. The catalyst (0.10 g), n-heptane (6.8 mmol), and benzene (1.2 mmol) were placed in a pressure tube with volume of 15 mL. The resulting mixture was then kept under stirring vigorously using a magnetic stir bar at 150 °C. After the completion of the reaction, the catalyst was separated by filtration, and quantitative and qualitative analyses were performed on the products using GC-FID and GC-MS. During the reaction, the pressure inside the reactor was approximately 4.5 \(\times\) 10\(^2\) kPa.

3. Results and Discussion

3.1. Characterization of Prepared Montmorillonite Catalysts

The results of the elemental analysis indicated that sodium was completely absent in H-mont and Al-mont (Na: < 0.01 mmol g\(^{-1}\)) after the ion-exchange treatment of Na-mont (Na: 0.86 mmol g\(^{-1}\)). The amount of Al in Al-mont was increased to 4.89 mmol g\(^{-1}\) from 4.40 mmol g\(^{-1}\) of aluminosilicate layer of Na-mont after the ion exchange. These indicate that almost all ion exchange sites of Al-mont are exchanged with Al cation. XRD patterns confirmed that the layered structure of montmorillonite was maintained after the ion exchange (Fig. 1). The shape of the XRD pattern of H-mont as well as the relative intensities of the peaks present (b) did not change significantly after the ultrasonic irradiation process ((c) and (d)) or the heat treatment (e), suggesting that the structural characteristics of H-mont were maintained after these treatments. On the other hand, the position of the d\(_{001}\) peak of H-mont (2\(\theta\) = 6-8°) shifted slightly after the ultrasonic irradiation process.

Fig. 1 XRD Patterns of (a) Na-mont, (b) H-mont, (c) H-mont(ui-0.5), (d) H-mont(ui-1.0), (e) H-mont(150), and (f) Al-mont
tion process as well as the heat treatment. The interlayer distances of the montmorillonite catalysts were calculated by subtracting the ε value of the silicate sheet (9.6 Å) from the d001 value as determined from the XRD pattern (Table 1). The interlayer distance of H-mont (5.0 Å) decreased after the treatment at 150 °C (H-mont(150): 2.5 Å) and the ultrasonic irradiation process (H-mont(ui): 3.0-3.9 Å). In the XRD pattern, as the d001 peak shifts, the d001 peak intensity also weakens. In the case of H-mont(ui-1.0), d001 peak shape was slightly changed with small amount of impurity peaks around 15-18 degree. It is considered that a part of the layered structure of H-mont was decomposed by ultrasonic irradiation, resulting the decrease of its interlayer distance. The interlayer distance of Al-mont (6.0 Å) was slightly higher than those of the H-mont samples, suggesting the presence of hydrated Al species within the montmorillonite interlayer in the case of the former.

### 3.2 Alkylation of Benzene with n-Heptane over Various Acid Catalysts

The performances of the various catalysts were compared at 150 °C for 16 h using n-heptane and benzene (Table 2). While H-mont showed catalytic activity for the alkylation reaction, the reaction did not proceed when Na-mont was used, indicating that the acid sites generated by the ion-exchange process are involved in the reaction. The benzene conversion increased after the ultrasonic irradiation process and heat treatment, and the Ph-C7 selectivity was maintained. The benzene conversion increased with the ultrasonic irradiation time in the case of H-mont(ui), and the Ph-C7 selectivity was ca. 70 %. H-mont(150) exhibited a benzene conversion of 0.91 %, and the Ph-C7 selectivity was 56 %. The benzene conversion improves by the heat treatment and ultrasonic irradiation of the parent H-mont layers decreases. This is probably because the decrease of adsorbed water on the active site of the catalyst. Similar phenomena were observed in Friedel-Crafts alkylation with a styrene derivative. With respect to the other alkylation products, the t-butylbenzene (Ph-t-C4) selectivity was 5 % in the case of H-mont, while the main Ph-C4 product was 2-phenylbutane in the case of H-mont(150).

When the reaction was performed using H-ZSM-5, the selectivities for the Ph-C7 and Ph-C3 products were 29 % and 64 %, respectively. The higher acid strength of Al-mont and H-ZSM-5 compared to H-mont might be induced the higher benzene conversion of Al-mont and H-ZSM-5 because of the difficulties of alkane activation. Regarding the byproduct, hydrogen was detected in the gas phase after the reaction. In addition, when H-mont and Al-mont were reused, we have confirmed the progress of the reaction although the catalytic activity was slightly reduced (H-mont: 0.24 % conv., 58 % selectivity to Ph-C7; Al-mont: 1.48 % conv., 83 % selectivity to Ph-C7).

The selectivities of the main products (Ph-C7, Ph-C3, and Ph-t-C4) were plotted against the benzene conversion to elucidate the reaction paths of the catalysts (Fig. 2). In the case of H-mont, the selectivity of Ph-t-C4 was high initially. Further, the selectivity of the target Ph-C7 product improved as the reaction progressed (Fig. 2(a)). The formation of Ph-t-C4 was also detected initially in the cases of H-mont(ui-0.5)

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**Table 1** Interlayer Distance of Cation-exchanged Montmorillonite Samples

| Sample          | 2θ [degree] | Interlayer distance [Å] |  
|-----------------|-------------|--------------------------|
| H-mont          | 6.0         | 5.0                      |
| H-mont(ui-0.5)  | 6.5         | 3.9                      |
| H-mont(ui-1.0)  | 7.0         | 3.0                      |
| H-mont(150)     | 7.3         | 2.5                      |
| Al-mont         | 5.7         | 6.0                      |
| Na-mont         | 7.2         | 2.7                      |

a) Determined by subtracting ε value of silicate sheet (9.6 Å) from d001 value determined from XRD spectrum shown in Fig. 1.

**Table 2** Solid-acid-catalyzed Alkylation of Benzene with n-Heptane

| Catalyst          | Benzene conv. [%] | Selectivity [%]       |
|-------------------|-------------------|-----------------------|
|                   |                   | Ph-C7  | Ph-C2  | Ph-C3  | Ph-t-C4 | Other Ph-C4 | Others |
| H-mont            | 0.38              | 59     | 7     | 4      | 5      | 2          | 23     |
| H-mont(ui-0.5)    | 0.75              | 71     | 8     | 4      | 1      | 1          | 15     |
| H-mont(ui-1.0)    | 0.87              | 69     | 6     | 4      | 1      | 2          | 18     |
| H-mont(150)       | 0.91              | 56     | 3     | 8      | 1      | 21         | 11     |
| Al-mont           | 1.82              | 58     | 21    | 5      | <1     | 2          | 14     |
| H-ZSM-5           | 1.74              | 29     | 1     | 64     | 1      | 3          | 2      |
| Na-mont           | 0.00              | -      | -     | -      | -      | -          | -      |

a) Reaction conditions: n-heptane (6.8 mmol), benzene (1.2 mmol), 150 °C, 16 h.
b) Other alkylbenzenes and diphenylmethane were mainly formed as other products. Selectivity to coke formation was less than 1 %.
and H-mont(ui-1.0) (Figs. 2(b) and 2(c)). However, the selectivity of Ph-t-C4 was much lower than that of the parent, H-mont. In the case of H-mont(150), the target, Ph-C7, was obtained with high selectivity right from the start of the reaction (Fig. 2(d)). This phenomenon was observed in the case of Al-mont as well, which also showed high Ph-C7 selectivity (Fig. 2(e)).

The H-ZSM-5 catalyst primarily afforded Ph-C3 and Ph-C7, and the selectivities of these products during the reaction maintained (Fig. 2(f)), suggesting that the catalytic properties of H-ZSM-5 remained stable over the course of the reaction.

The sharp changes in the product selectivity in the case of H-mont can be explained by the changes in the catalyst structure during the reaction. The initial Ph-t-C4 selectivity was correlated with the interlayer distance of H-mont; the selectivity decreased with a decrease in the order of magnitude of the interlayer distance of H-mont, as shown in Table 1. For example, the Ph-t-C4 selectivity in the case of H-mont (interlayer distance: 5.0 Å) for a conversion of 0.04 % was 37 % while for H-mont(ui-1.0; interlayer distance: 3.0 Å), it was 19 % for a conversion of 0.05 %. To investigate the structural changes induced in H-mont during the reaction, the H-mont sample was recovered after each conversion process and subjected to XRD measurement. The benzene conversion and the corresponding interlayer distances were as follows: 0.04 %, 2.4 Å; 0.07 %, 1.3 Å; and 0.38 %, 0.9 Å. From these results, it can be surmised that the interlayer distance of H-mont decreased with an increase in the Ph-C7 selectivity, as the reaction progressed. On the other hand, although Al-mont exhibited the same interlayer distance as H-mont before the reaction, the target Ph-C7 product was obtained with high selectivity right from the beginning (Fig. 2(e)). This suggests that its selectivity did not depend on the interlayer distance of Al-mont, in contrast to the case for H-mont. During the reaction, the interlayer distance of Al-mont and H-mont(ui-0.5) decreased to 2.6 Å and 3.2 Å, respectively, so it seems that the interlayer distance generally decreases after the reaction.

In order to investigate the initial and secondary reactions based on the products obtained, the product selectivities for a benzene conversion of approximately 1 % were evaluated. Table 3 shows the isomer distribution for the Ph-C7 product for the different catalysts. Structures of main Ph-C7 isomers are shown in Fig. 3. When montmorillonite was used as the catalyst, selectivity was observed in each isomer. On the other hand, when H-ZSM-5 was used, the selectivity for 2-phenylheptane was high, while 3-phenylheptane and 4-phenylheptane were not detected. This was probably because of the molecular sieving effect of the micropores of H-ZSM-5. Previous studies on the reaction between hexane and benzene over H-ZSM-5 have reported that 1-phenylheptane is produced during the reaction\(^{19,20}\). However, in the case of our reaction system investigated in the present study, the formation of 1-phenylheptane was not confirmed. As shown in Fig. 4, the Ph-C7

![Fig. 2 Product Selectivities vs. Benzene Conversion for Alkylation Reaction of n-Heptane over (a) H-mont, (b) H-mont(ui-0.5), (c) H-mont(ui-1.0), (d) H-mont(150), (e) Al-mont, and (f) H-ZSM-5](image)
isomer distribution did not change significantly as the reaction progressed. These results indicate that the reaction proceeded because of carbocation and that the initially generated Ph-C7 product did not undergo isomerization.

As shown in Fig. 5, the selectivities of ethylbenzene (Ph-C2) and 2-phenylbutane increased after an increase in the reaction time. These results indicate that the main reason for the decrease in the Ph-C7 selectivity for benzene conversion higher than 0.5% was the secondary cracking reaction of Ph-C7. When the catalysts that were not preheated before the reaction, namely, H-mont, H-mont(0.5), H-mont(1.0), and Al-mont, were used, the selectivity of ethylbenzene increased as the reaction progressed (Fig. 5(A), data for H-mont). On the other hand, when H-mont(150), which was preheated before the reaction, was used, the selectivity of 2-phenylbutane (Ph-C4(2)) increased (Fig. 5(B)). However, the reason for the observed differences in the selectivities of the byproducts is not clear.

3.3. Proposed Alkylation Reaction Mechanism
The isomer distribution of the Ph-C7 product (Table 3) implies that a carbocation mechanism is involved. The Ph-C7 product could be obtained by a bimolecular reaction between the C7 alkyl cation and benzene, while Ph-C(4) and Ph-C(3), the initial products in the cases of H-mont and H-ZSM-5 (Figs. 2(a) and 2(f)), respectively, were formed after the monomolecular cracking of heptane. When the interlayer distance is small (ca. 2-3 Å), owing to the progress of the mont-catalyzed reaction, a heat-based drying pretreatment (H-mont(150)), or ultrasonic irradiation (H-mont(ui)), the reaction primarily occurs at the edge and/or surface of the montmorillonite particles because both n-heptane and benzene cannot penetrate through the small interlayer space. As a result, the bimolecular reaction proceeds primarily because of the less-sterically hindered environment to selectively yield the Ph-C7 products ((A) in Scheme 1).

This hypothesis is supported by the isomer distribution data. As shown in Table 3, the distribution of the Ph-C7 isomers changed as the reaction progressed. These results indicate that the reaction proceeded because of carbocation and that the initially generated Ph-C7 product did not undergo isomerization.

### Table 3: Distribution of Ph-C7 Isomer during Reaction of n-Heptane and Benzene for Benzene Conversion of 1%}

| Catalyst          | Benzene conv. [%] | Ph-C7 selectivity [%] | Ph-C7 isomer distribution [%] |
|-------------------|-------------------|-----------------------|-------------------------------|
|                   |                   | Ph-C7(2) | Ph-C7(3) | Ph-C7(4) | Ph-C7(others) |
| H-montb)          | 1.16              | 29      | 22      | 13      | 36           |
| H-mont(ui-0.5)    | 0.75              | 31      | 24      | 11      | 34           |
| H-mont(ui-1.0)    | 0.87              | 32      | 26      | 13      | 30           |
| H-mont(150)       | 0.91              | 31      | 16      | 7       | 46           |
| H-ZSM-5c)         | 0.77              | 42      | 0       | 0       | 58d)         |

a) Reaction conditions: n-heptane (6.8 mmol), benzene (1.2 mmol), 150 °C.  
b) 64 h.  
c) 6 h.  
d) Other Ph-C7 products primarily included (dimethylcyclopentyl)benzene.
the fact that the order of magnitude of the Ph-t-C4 selectivity in the initial stage of the reaction corresponds to the respective interlayer distances of H-mont, H-mont (ui-0.5), H-mont(ui-1.0), and H-mont(150) (Table 1 and Figs. 2(a)-2(d)). The yield of Ph-t-C4 peaked at 6 h and then decreased with the progress of the reaction. Olah and coworkers have reported that alkylbenzene is also protonated by an acid catalyst and that the corresponding carbocation is formed, followed by hydride transfer from the other alkanes to the carbocation, yielding another alkylbenzene²¹. A few alkylbenzene products may be formed from Ph-t-C4 if the reaction time is high. In the case of H-ZSM-5, the monomolecular cracking of n-heptane was also observed. The high selectivity of H-ZSM-5 toward Ph-C3 can be ascribed to the molecular sieving effect ((C) in Scheme 1). As shown in Table 3, 3-phenylheptane and 4-phenylheptane were not formed during the H-ZSM-5-catalyzed reaction. This result also supports the conclusion that a smaller pore size preferentially affords small-molecular-diameter products and that Ph-C3 is the other initial product formed along with Ph-t-C4 in the case of H-ZSM-5³⁷).

In the case of Al-mont, the target Ph-C7 product was obtained with high selectivity right from the beginning, even though Al-mont has the same interlayer distance as H-mont. It is thought that, in the case of Al-mont, the degree of steric hindrance and hydrophilicity of the

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Fig. 5 Selectivities of Ph-C7 (●), Ethylbenzene (Ph-C2) (▲), and 2-Phenylbutane (Ph-C4(2)) (■) vs. Benzene Conversion: (a) H-mont and (b) H-mont(150)

Scheme 1 Proposed Alkylation Reaction Mechanism in Case of (A) Mont Surface, (B) H-mont with Large Interlayer Distance, and (C) H-ZSM-5
interlayer are increased because of the presence of Al$^{3+}$ cations, which prevents the insertion of the substrate into the interlayers. The almost complete ion exchange ratio to Al from Na also support this hypothesis. Therefore, the bimolecular reaction occurs preferentially at the surfaces or edges of the Al-mont particles, as shown in Fig. 6.

When a mont-based catalyst was used, the cracking reaction of Ph-C7 resulted in a benzene conversion of 0.5%, and ethylbenzene and 2-phenylbutane are formed as the by-products (Fig. 5). On the other hand, when ZSM-5 was used, the selectivity of the product did not change even when the reaction time was prolonged till the benzene conversion was more than 1%. This indicates that almost no secondary reaction involving the product had occurred. This is presumably because the product barely diffused into the pores of the zeolite, because of which the secondary reaction was suppressed.

H-mont has a lower acid strength than those of Al-mont and H-ZSM-5$^{(5),(17)-(30)}$, therefore, the bimolecular reaction affording Ph-C7 preferentially occurs compared to monomolecular cracking of n-heptane. On the other hand, carbocation from the desired product, Ph-C7, is more stable than that from simple alkane, resulting the cracking reaction of Ph-C7 to ethylbenzene and 2-phenylbutane at more than 1% conversion of benzene. Although Al-mont and H-ZSM-5 have comparable acid strengths$^{(5),(17)-(30)}$, the product selectivities of these two catalysts were significantly different. This fact strongly supports that the structure of the catalyst, not the acid strength, determines the product selectivity.

**4. Conclusion**

Proton-exchanged montmorillonite (H-mont) as catalyst was prepared by an ion-exchange procedure. After the H-mont catalyst had been subjected to heat-based drying and ultrasonic irradiation, the activity and selectivity of the Ph-C7 product during the reaction between n-heptane and benzene increased. Detailed time-course analysis of the H-mont-catalyzed alkylation reaction helped to elucidate the reaction pathways, which are affected by the mont interlayer spacing. It was found that the bimolecular reaction occurs preferentially on the catalyst surface when the interlayer spacing is very small. On the other hand, monomolecular cracking occurs to yield a tertiary cation when the spacing is large. Aluminum-exchanged montmorillonite (Al-mont) and H-ZSM-5 also showed catalytic activity during the direct alkylation of benzene to yield Ph-C7 and Ph-C3, respectively. Thus, direct, noble-metal-free mont-catalyzed alkylation would allow for the efficient use of alkanes.

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要 旨
プロトン交換モンモリロナイト触媒を用いたn-ヘプタンによるベンゼンの液相直接アルキル化の反応機構

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固体酸触媒であるモンモリロナイトを用いたときのn-ヘプタンによるベンゼンの直接アルキル化における反応機構を調査した。プロトン交換モンモリロナイトやアルミニウム交換モンモリロナイトが本反応に活性を示すことが分かった。また、プロトン交換モンモリロナイトの触媒活性は、加熱や超音波照射などの前処理によって増加し、反応初期の生成物の選択性も変化した。生成物選択性の詳細な経時変化の測定によって、層間がより狭い触媒の場合、表面で二分子反応が優先的に起こり、高い選択性で目的の炭素鎖7のアルキル化生成物が得られることが明らかになった。一方、前処理を行っていない層間が広いプロトン交換モンモリロナイトでは、層間におけるn-ヘプタンの単分子クラックングにより、i-ブチルカチオンが生じ、i-ブチルベンゼンが生成した。H-ZSM-5を触媒として使用した場合もn-ヘプタンの単分子クラックングが起きるが、主生成物はイソプロピルベンゼンとなった。