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Cation-Exchanged Montmorillonite-Catalyzed Friedel–Crafts Transannular Alkylation with (*Z*,*Z*)-1,5-Cyclooctadiene

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Synopsis. The five isomers of phenylbicyclooctanes were produced by Friedel–Crafts transannular alkylation of benzene with (*Z*,*Z*)-1,5-cyclooctadiene (1,5-COD) in the presence of a cation-exchanged montmorillonite (M^{n+}-mont). M^{n+}-Mont could be used repeatedly to provide the same products in good yields.

Some of us reported recently that five or six isomers of phenylbicyclooctanes were produced in the alkylation of benzene with (*Z*,*Z*)-1,5-cyclooctadiene (abbreviated to 1,5-COD) in the presence of various acid catalysts such as $AlCl_3$, $MoCl_5$, and concd H_2SO_4.[1)] Cation-exchanged montmorillonite (abbreviated to M^{n+}-mont), a kind of modified natural clay, is known to behave as both a Brönsted acid and a Lewis acid and it has been used as a catalyst for many organic reactions such as addition, elimination, rearrangement, and Friedel–Crafts reactions.[2)] Advantages of the catalyst are easy handling, chemical inertness (noncorrosiveness), low cost, and easy modification of acidity by exchanging the cations in the interlayer space.[2,3)] We have become interested in the catalytic use of various M^{n+}-mont for organic synthesis[4)] and the results of application of these catalysts to the above Friedel–Crafts alkylation of benzene with 1,5-COD will be reported here.

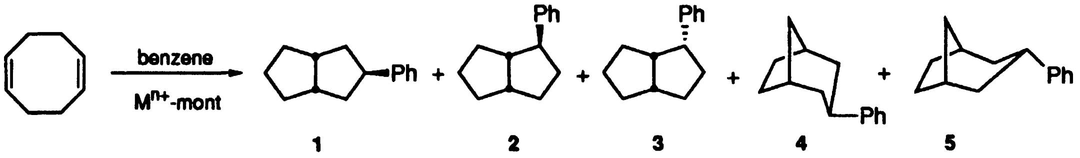
Friedel–Crafts transannular alkylation of benzene, which was used as the reactant as well as the solvent, with 1,5-COD was done in the presence of Al^{3+}-mont at reflux temperature to produce the isomeric phenylbicyclooctanes **1**—**5** (Scheme 1, Table 1). At lower temperature the reaction was quite slow. The compounds **1**—**5** were obtained with a low product selectivity and *endo*-3-phenyl-*cis*-bicyclo[3.3.0]octane **6** (Chart 1), the thermodynamically most stable isomer,[1)] was not obtained under the conditions used. On the other hand, in the alkylation of benzene with 1,5-COD by use of $AlCl_3$, compound **6** was formed appreciably by isomerization of the compounds **1**—**5**.[1)] This shows that Al^{3+}-mont does not have the ability for such isomerization and is a milder catalyst than $AlCl_3$. The product yield depended much on the nature of M^{n+}-mont and the best yield was obtained in the reaction catalyzed by Fe^{3+}- and Zn^{2+}-mont, followed by that using Ce^{3+}-, Al^{3+}-, and Zr^{4+}-mont (Table 2).

We estimated the amount of active acid sites on M^{n+}-mont by poisoning it with triethylamine in the alkylation system following and slightly modifying the previously reported method.[5)] In the alkylation with Al^{3+}-, Ce^{3+}-, or Zn^{2+}-mont (500 mg), the addition of 0.319, 0.078, or 0.186 mmol of triethylamine stopped the reaction completely, respectively. This result indicates that the amount of active acid sites is 0.638 $mmol\,g^{-1}$ on Al^{3+}-mont, 0.156 $mmol\,g^{-1}$ on Ce^{3+}-mont, and 0.372 $mmol\,g^{-1}$ on Zn^{2+}-mont. The turnover number was calculated as 3, 13, and 6 on the basis of the amount of active acid sites on Al^{3+}-, Ce^{3+}-, and Zn^{2+}-mont, respectively. The amount of acid sites on M^{n+}-mont was also estimated from the amount of adsorbed NH_3 gas at 100 °C by the temperature-programmed desorption of NH_3 gas (NH_3-TPD) and that on Al^{3+}-, Ce^{3+}-, and Zn^{2+}-mont was estimated to be 0.531, 0.141, and 0.371 $mmol\,g^{-1}$, respectively.[4b)]

For comparison, the reactions with other solid acid catalysts such as Amberlyst® 15 (cation exchange resin) and Nafion® NR50 (perfluorinated resin)[6)] were also done. Similar alkylation occurred to afford the compounds **1**—**5** in high yields at the reflux temperature of benzene, where compound **1** was obtained with good selectivity as in the case of H_2SO_4 catalyst (Table 2).

It has been known that Fe^{3+}-mont can be used repeatedly in the benzylation of toluene.[7)] We also found that M^{n+}-mont has the advantage of reuse in this alkylation (Table 3). New Al^{3+}-mont was white, while the recovered Al^{3+}-mont was gray. Interestingly, the product yield increased in the presence of the recovered Al^{3+}-mont (Table 3, Run 2), and the result was reproducible. One possible explanation for this is that water included in strongly acidic Al^{3+}-mont may be removed by azeotropic distillation with benzene in the first reaction to yield a highly active Al^{3+}-mont for the 2nd use.[8)] Zn^{2+}-Mont could be regenerated to produce the same products, while a weakly acidic Ce^{3+}-mont could not be regenerated well for the third use. On the other hand, the product yield did not decrease appreciably upon use of the recovered Nafion® NR50 (Table 3, Runs 11 and 12), but in the Amberlyst® case the catalyst decomposed and was not reusable. Although Nafion® NR50 showed similar reactivity and usefulness as M^{n+}-mont in this reaction, the merits for M^{n+}-mont may be found in its lower cost and safety from the environmental viewpoint.

In this alkylation an initially produced electrophile is probably a *cis*-bicyclo[3.3.0]octyl cation **a** which may isomerize to the cations **b** and **c** (Scheme 2). The cations can be stabilized by negative charge of oxygens on the surface of M^{n+}-mont and attack benzene elec-



Scheme 1.

Table 1. Product Yield and Ratio in Al^{3+}-Mont-Catalyzed Friedel–Crafts Transannular Alkylation of Benzene with 1,5-COD[a)]

Run	Conditions		Isolated	Product ratio/%[c)]				
	Temp/°C	Time/h	yield/%[b)]	**1**	**2**	**3**	**4**	**5**
1	80[d)]	24	38	26	24	11	19	20
2	60	240	20	23	22	16	19	20
3[e)]	42[d)]	456	16	16	31	18	22	13
4	R.T.	24	0	—	—	—	—	—

a) 1,5-COD (30 mmol), benzene (30 cm^3), Al^{3+}-mont (750 mg, 0.479 mmol as an active acid site). b) Based on 1,5-COD. c) GLC area ratio. d) Reflux temperature. e) A mixture of benzene (10 cm^3) and CH_2Cl_2 (20 cm^3) as solvent.

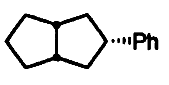


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Chart 1.

Table 2. Product Yield and Ratio in Friedel–Crafts Transannular Alkylation of Benzene with 1,5-COD in the Presence of M^{n+}-Mont or Resin Catalyst[a)]

Run	Catalyst	Isolated	Product ratio/%[c)]					
		yield/%[b)]	**1**	**2**	**3**	**4**	**5**	**6**
1	Zr^{4+}-mont	25	27	25	15	18	15	0
2	Al^{3+}-mont	32	27	25	15	19	14	0
3	Fe^{3+}-mont	45	33	24	10	19	14	0
4	Ce^{3+}-mont	39	31	26	12	19	12	0
5	Zn^{2+}-mont	45	28	26	14	20	12	0
6	Ca^{2+}-mont	8	13	29	32	20	6	0
7	Mg^{2+}-mont	27	24	26	25	17	8	0
8	Na^{+}-mont	0	—	—	—	—	—	—
9	$AlCl_3$ [d)]	60	2	47	6	23	2	20
10	Amberlyst® 15[e)]	6	13	14	61	9	3	0
11	Amberlyst® 15	53	59	15	5	11	10	0
12	Nafion® NR50[e)]	1	33	20	29	14	4	0
13	Nafion® NR50	58	62	17	6	11	4	0
14	concd H_2SO_4[f)]	55	58	21	3	16	2	0

a) 1,5-COD (2.54 mmol), benzene (10 cm^3), catalyst (500 mg); at reflux temperature for 24 h. b) Based on 1,5-COD. c) GLC area ratio. d) 1,5-COD (20 mmol), benzene (50 cm^3), $AlCl_3$ (10 mmol); at 25 °C for 3 h. e) Reaction temperature, 60 °C. f) 1,5-COD (20 mmol), benzene (50 cm^3), H_2SO_4 (20 mmol); at 25 °C for 2 h.

Table 3. Product Yield and Ratio in Friedel–Crafts Transannular Alkylation of Benzene with 1,5-COD in the Presence of Recycled M^{n+}-Mont or Nafion® NR50[a)]

Run	Catalyst	Isolated	Product ratio/%[c)]				
		yield/%[b)]	**1**	**2**	**3**	**4**	**5**
1	Al^{3+}-mont (1st use)	32	27	25	15	19	14
2	Al^{3+}-mont (2nd use)	69	38	26	5	20	11
3	Al^{3+}-mont (3rd use)	56	37	24	6	20	13
4	Ce^{3+}-mont (1st use)	39	31	26	12	19	12
5	Ce^{3+}-mont (2nd use)	31	32	25	11	19	13
6	Ce^{3+}-mont (3rd use)	19	29	27	13	19	12
7	Zn^{2+}-mont (1st use)	45	28	26	14	20	12
8	Zn^{2+}-mont (2nd use)	47	27	25	12	21	15
9	Zn^{2+}-mont (3rd use)	40	26	27	14	22	11
10	Nafion® NR50 (1st use)	58	62	17	6	11	4
11	Nafion® NR50 (2nd use)	60	66	17	6	8	3
12	Nafion® NR50 (3rd use)	53	62	17	6	11	4

a) 1,5-COD (2.54 mmol), benzene (10 cm^3), catalyst (500 mg); at reflux temperature for 24 h. b) Based on 1,5-COD. c) GLC area ratio.

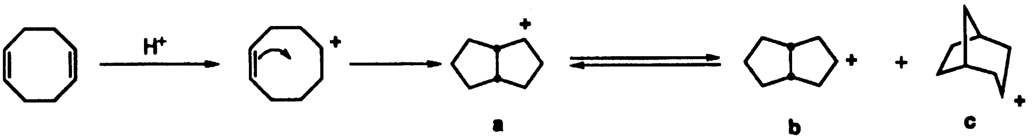
trophically to produce the compounds **1**—**5**. The formation of **1** rather than **6** from the cation **b** seems to be kinetically favored by considering the direction of attack of benzene to **b**.

In conclusion, although the yield as well as the product selectivity was not improved in this M^{n+}-mont-catalyzed reaction compared with the $AlCl_3$- or H_2SO_4-catalyzed one, it was disclosed that various M^{n+}-mont worked as a catalyst for Friedel–Crafts transannular alkylation with 1,5-COD for the first time where easy separation of the catalyst from the reaction mixture, a convenient work-up procedure, and the reusability of the catalyst are the merits.

Experimental

GLC analyses were done on a Shimadzu GC-14A instrument (25 m×0.33 mm, 5.0-μm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with a flame-ionization detector and He as carrier gas. Column chromatography on SiO_2 was done with Wakogel® C-200 and C-300 using hexane as eluent. X-Ray powder diffraction (XRD) data were obtained on a Shimadzu XD-D1 diffractometer using Cu $K\alpha$ radiation and an energy dispersive detector.

All commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the usual method before use. Kunipia® G, namely Na^+-mont, was obtained from Kunimine Industries Co., Ltd. M^{n+}-Mont ($M^{n+}=Zr^{4+}$, Al^{3+}, Fe^{3+}, and Zn^{2+}) was prepared by treatment of Na^+-mont with the corresponding metal oxychloride or nitrate in aqueous acetone as described separately.[4)] The basal spac-



Scheme 2.

ings (d_{001}) of Al^{3+}- and Zn^{2+}-mont were measured by a sharp peak obtained on XRD analyses as 12.5 and 14.9 Å, respectively, showing clearly that the catalysts have an interlayer structure. On the other hand, those of Zr^{4+}- and Fe^{3+}-mont were measured by a broad peak as >18 Å indicating that the catalysts might have either an interlayer structure or a random structure. Additionally, $Ce(NO_3)_3 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ were used as the cation source, respectively, for Ce^{3+}-, Ca^{2+}-, and Mg^{2+}-mont. The color of Ce^{3+}-, Ca^{2+}-, and Mg^{2+}-mont is white. The basal spacings of Ce^{3+}-, Ca^{2+}-, and Mg^{2+}-mont were measured by a sharp peak obtained on XRD analyses as 15.2, 14.9, and 14.6 Å, respectively. The amount of acid sites on Ce^{3+}-, Ca^{2+}-, and Mg^{2+}-mont was measured to be 0.141, 0.156, and 0.233 $\mathrm{mmol\,g^{-1}}$, respectively, by the temperature-programmed desorption of ammonia gas (NH_3-TPD) as mentioned previously.[4)]

Measurement of the Amount of Active Acid Sites on M^{n+}-Mont with Triethylamine-Doped Benzene. A typical example using Zn^{2+}-mont is described below. Following and slightly modifying a method from the literature,[5)] a mixture of triethylamine-doped benzene (10 cm^3) and Zn^{2+}-mont (500 mg) was stirred magnetically at 25 °C for 12 h. To the mixture was added dropwise 1,5-COD (275 mg, 2.54 mmol). The mixture was raised to the reflux temperature of benzene during about 30 min with stirring and then stirred at the temperature for 24 h with monitoring by GLC. The amount of active acid sites was calculated by the amount of triethylamine which stopped the reaction completely.

General Procedure for Friedel–Crafts Transannular Alkylation of Benzene with (*Z*,*Z*)-1,5-Cyclooctadiene (1,5-COD) in the Presence of M^{n+}-Mont. A typical example using Zn^{2+}-mont is described below (Table 2, Run 5). A mixture of benzene (6 cm^3) and Zn^{2+}-mont (500 mg, 0.186 mmol as an active acid site) was stirred magnetically at 25 °C for 15 min. To the mixture was added dropwise a benzene solution (4 cm^3) of 1,5-COD (275 mg, 2.54 mmol). The mixture was raised to the reflux temperature of benzene during about 30 min with stirring and then stirred at the temperature for 24 h with monitoring by GLC. After it had been cooled, the catalyst was removed by filtration and washed with benzene (10 cm^3). Removal of the solvent and unreacted 1,5-COD from the filtrate by a rotary evaporator left a pale yellow oil which was chromatographed on a SiO_2 column to give a mixture of the five isomers of phenylbicyclooctanes as a colorless oil (212 mg, 1.14 mmol, 45% yield). Each isomer was identified by GLC analysis by comparison with the authentic compounds.[1)] The product ratio was calculated on the basis of the area ratio on GLC analysis.

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