Cation-Exchanged Montmorillonite (M^{n+}-Mont)-Catalyzed Prins Reaction

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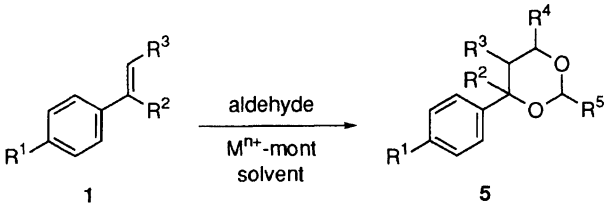
The Prins reaction of styrenes with paraformaldehyde or 1,3,5-trioxane in toluene in the presence of cation-exchanged montmorillonite (M^{n+}-mont), which worked as a Brønsted acid catalyst, at 80 °C produced 4-aryl-1,3-dioxanes selectively in up to 99% isolated yield with a turnover number of up to 5.9×10^2. Among the examined 21 M^{n+}-monts, Ce^{3+}- and Fe^{3+}-monts were revealed to be quite effective. Regeneration of the catalyst was confirmed with the Ce^{3+}-mont, which could be effectively recycled at least three times. Many lanthanide metal ion-exchanged montmorillonites (Ln^{3+}-monts) were prepared and characterized by X-ray powder diffraction (XRD) and temperature-programmed desorption of ammonia gas (NH_3-TPD) methods.

The organic transformation and improvement of the selectivity of reactions in the presence of a variety of solid catalysts are of recent interest, and many useful synthetic methods have been developed.[1,2] Currently, we have been much interested in the catalytic use of cation-exchanged clays as one of such catalysts for organic synthesis.[3,4] Since these clay catalysts might make the reaction processes comfortable and benign to Earth, they might act as substitutes for several homogeneous catalysts, because they have many conveniences, such as ease of handling, non-corrosiveness, low cost, regeneration, ready modification of the catalytic activity by cation-exchange in the interlayer space, and the reduction of unavoidable reaction wastes, such as aluminium salts and sulfuric acid. The Prins reaction, the acid-catalyzed addition of formaldehyde to alkenes, is known to be one of the typical electrophilic reactions,[5] the products of which are synthetically useful precursors of 1,3-diols.[6] Although such reactions have so far been investigated[7] using several solid catalysts, such as resin[8] and zeolite,[9] there are no examples of a Prins reaction in the presence of clays to the best of our knowledge. As one of our series of studies on clay-catalyzed organic synthesis, we report here on the result of our attempts to obtain a cation-exchanged montmorillonite (M^{n+}-mont)-catalyzed Prins reaction of styrenes with aldehydes, giving 1,3-dioxane derivatives.

Results and Discussion

Prins Reaction of Styrene (1a) with Paraformaldehyde-(2). Since it was observed that the treatment of styrene (**1a**) with paraformaldehyde (**2**) in toluene in the presence of Al^{3+}-mont[3b,3c] produced 4-phenyl-1,3-dioxane (**5a**), a search for optimization was first carried out using this mont catalyst. As a result, the use of a 1 mol% (18 wt%) catalyst in toluene at 80 °C for 6 h was revealed to be the condition of choice (Scheme 1, Table 1), in which the reaction proceeded smoothly to produce **5a** in 93% isolated yield with a turnover number of 1.9×10^2. Certainly, without the addition



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Scheme 1.

Table 1. Prins Reaction of Styrene **1a** with Paraformaldehyde **2**[a]

Run	Al^{3+}-Mont mg (mmol)[b]	Solvent	Temp °C	Time h	Isolated yield of **5a**/%[c]	TON[d]
1	94.2, (0.05)	Toluene	100	6	76	7.6×10
2	94.2, (0.05)	Toluene	80	2	72	7.2×10
3	94.2, (0.05)	Toluene	80	6	93	9.3×10
4	94.2, (0.05)	Toluene	80	12	93	9.3×10
5	94.2, (0.05)	Toluene	60	6	83	8.3×10
6	94.2, (0.05)	Toluene	25	6	0	0
7	9.4, (0.005)	Toluene	80	6	19	1.9×10^2
8	0 (0)	Toluene	80	6	0	—
9	94.2, (0.05)	Dioxane	80	12	77	7.7×10
10	94.2, (0.05)	Benzene	80	6	76	7.6×10
11	94.2, (0.05)	DME	80	6	37	3.7×10

a) **1a** (5 mmol), **2** (10 mmol), and solvent (10 cm^3). b) The number of acid sites (see Experimental section). c) Based on **1a**. d) Turnover number: based on the number of acid sites.

of Al^{3+}-mont, no reaction took place. At higher temperature the reaction was accompanied by an undesired formation of tarry products, while at 25 °C no reaction occurred. With 0.1 mol% (1.8 wt%) catalyst the reaction was slow and the product yield became low. As for the solvents, although benzene, 1,4-dioxane, and 1,2-dimethoxyethane (DME) could also be used, the reaction hardly occurred in polar or coordinating solvents, such as *N*,*N*-dimethylformamide (DMF), methanol, ethanol, acetonitrile, and water.

The catalytic activity of a variety of M^{n+}-monts other than Al^{3+}-mont for this Prins reaction was then examined (Table 2). Commercially available H^+-mont (in this case, montmorillonite K10 or H_2SO_4-treated clay) was found to be effective for this reaction. Ce^{3+}- and Fe^{3+}-monts were proven to be most effective for this reaction, providing **5a** in over 90% yield with turnover numbers of up to 5.9×10^2. At the same time, trace amounts of by-products (supposed to be 1-phenyl-1-tolylethane, 3-phenyl-2-propen-1-ol, and styrene dimers) were detected by GLC and GC-MS. The order of the catalytic efficiency of M^{n+}-monts was roughly estimated as follows from the product yield and the turnover number: Ce^{3+}-, Fe^{3+}-> Dy^{3+}-> H^+-$\gg Al^{3+}$-, La^{3+}-, Pr^{3+}-, Nd^{3+}-, Eu^{3+}-> Tb^{3+}-, Ho^{3+}-, Gd^{3+}-, Mg^{2+}-, Zr^{4+}-, Zn^{2+}-, Ca^{2+}-, Y^{3+}-, Sm^{3+}-> Er^{3+}-, Yb^{3+}-> Na^+-mont. Although the reason is not yet known, it is noteworthy that Dy^{3+}-mont was remarkably active for this reaction among many lanthanide ion-exchanged montmorillonites (Ln^{3+}-monts). The order of the catalytic efficiency of M^{n+}-monts was also estimated as follows from the product yield per weight of the catalyst: Fe^{3+}-> H^+-> Al^{3+}-> Ce^{3+}-$\gg Zr^{4+}$-, La^{3+}-, Dy^{3+}-, Pr^{3+}-, Zn^{2+}-, Nd^{3+}-, Eu^{3+}-, Tb^{3+}-, Ho^{3+}-, Y^{3+}-, Gd^{3+}-, Mg^{2+}-, Sm^{3+}-, Ca^{2+}-> Er^{3+}-, Yb^{3+}-> Na^+-mont. In this estimation Fe^{3+}-mont was again more effective than H^+-mont and Al^{3+}- and Ce^{3+}-monts were effective as well as H^+-mont. The effectiveness of Ce^{3+}-, Fe^{3+}-, and Al^{3+}-monts has so far been found in several clay-catalyzed organic reactions, such as the acetalization of carbonyl compounds,[3e] Friedel–Crafts alkylation,[3a] and a rearrangement of alkyl phenyl ethers to alkylphenols.[3b]

Table 2. Effect of M^{n+}-Mont for Prins Reaction of **1a** with **2**[a]

Run	M^{n+}-Mont			Isolated yield of **5a**/%[c]	TON[d]
		mg	(mmol)[b]		
1	Zr^{4+},	68.1	(0.05)	50	5.0×10
2	Fe^{3+},	143.3	(0.05)	93	9.3×10
3	Fe^{3+},	14.3	(0.005)	58	5.8×10^2
4	Y^{3+},	15.9	(0.005)	4	3.8×10
5	La^{3+},	25.0	(0.005)	16	1.6×10^2
6	Ce^{3+},	354.6	(0.05) 1st	90	9.0×10
7	Ce^{3+},	354.6	(0.05) 2nd	86	8.6×10
8	Ce^{3+},	354.6	(0.05) 3rd	85	8.5×10
9	Ce^{3+},	10.6	(0.0015)	18	5.9×10^2
10	Pr^{3+},	35.7	(0.005)	15	1.5×10^2
11	Nd^{3+},	40.0	(0.005)	14	1.4×10^2
12	Sm^{3+},	18.2	(0.005)	4	3.8×10
13	Eu^{3+},	45.9	(0.005)	14	1.4×10^2
14	Gd^{3+},	20.0	(0.005)	5	5.2×10
15	Tb^{3+},	24.5	(0.005)	7	6.6×10
16	Dy^{3+},	84.7	(0.005)	53	5.3×10^2
17	Ho^{3+},	23.1	(0.005)	6	5.6×10
18	Er^{3+},	18.8	(0.005)	1	1.2×10
19	Yb^{3+},	15.5	(0.005)	0.5	5
20	Mg^{2+},	214.6	(0.05)	51	5.1×10
21	Ca^{2+},	320.5	(0.05)	44	4.4×10
22	Zn^{2+},	134.8	(0.05)	50	5.0×10
23	H^+,[e]	157.7	(0.05)	93	9.3×10
24	H^+,[e]	15.8	(0.005)	47	4.7×10^2
25	Na^+,	500.0	(0)	0	—

a) **1a** (5 mmol), **2** (10 mmol), and toluene (10 cm^3) at 80 °C for 6 h. b) The number of acid sites (see Experimental section). c) Based on **1a**. d) Based on the number of acid sites. e) Montmorillonite K10, Aldrich Chemical Co., Inc.

It was clarified that Ce^{3+}-mont maintained its own layer structure during the reaction, since the recovered Ce^{3+}-mont had the same basal spacing (d_{001}) of 15.2 Å based on a X-ray diffraction (XRD) analysis, compared with that of freshly prepared Ce^{3+}-mont. This means that the interlayer space of Ce^{3+}-mont is approximately 5.6 Å or more apart, and is enough to enable both substrates, **1a** and **2**, to enter between the two layers. On the other hand, a d_{001} of Fe^{3+}-mont was not obtained by an XRD analysis after the reaction, and the interlayer structure was not determined. Additionally, after the reaction in the presence of either Ce^{3+}- or Fe^{3+}-mont, such cations were not detected in the reaction supernatant by X-ray fluorescence (XRF) analyses, showing that the cations were evidently not removed from the surface of Ce^{3+}- or Fe^{3+}-mont. It is worth noting that the recovered Ce^{3+}-mont could not be reused for this reaction as such, but was successfully regenerated and reused at least three times after washing with aqueous acetone and successive drying at 120 °C.

The number of acid sites (Brønsted and also Lewis acid sites) of these M^{n+}-monts was tentatively estimated for convenience by the previously described temperature-programmed desorption of the ammonia gas (NH_3-TPD) method.[3a] Although the number of acid sites in the M^{n+}-mont determined by NH_3-TPD may not accurately represent the active acid sites available to this reaction, it provides a reference for M^{n+}-mont acidity. Here, another attempt for estimating the number of acid sites of M^{n+}-mont, in this case, Ce^{3+}-mont, by poisoning the reaction system with triethylamine[3d,3e,10] failed because the reaction system was not completely poisoned to stop the reaction, even by using excess triethylamine (Fig. 1). M^{n+}-monts are well-known to act as both a Brønsted acid whose acid sites are derived from the coordination of water molecules to the exchanged cations in the interlayer space and a Lewis acid whose acid sites are exchanged cations and aluminium atoms of the framework of clay.[11] In this reaction Brønsted acid sites of M^{n+}-monts might act predominantly. The course of this M^{n+}-mont-catalyzed Prins reaction in the interlayer space is shown schematically in Scheme 2. Here, monomeric formaldehyde might be produced by the decomposition of **2** due to an interaction with the acid sites of the clay surface.

Prins Reaction of Styrenes (1) with Paraformaldehyde

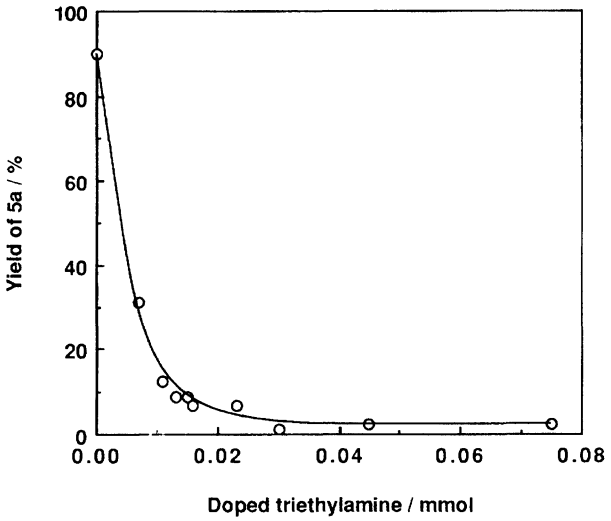
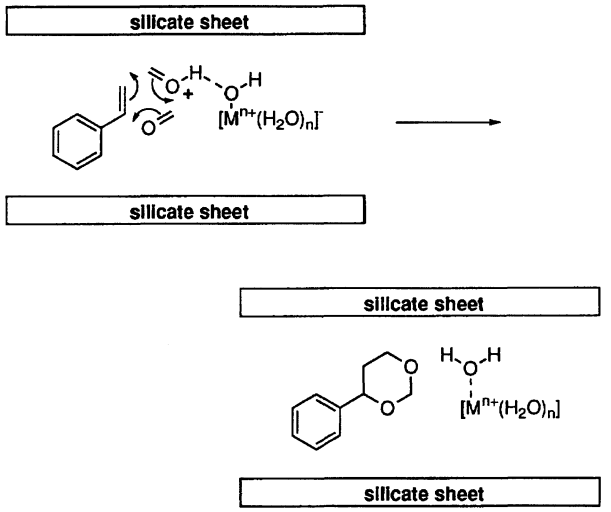


Fig. 1. The yield (○) of **5a** in Prins reaction of **1a** (5.00 mmol) with **2** (10.0 mmol) in the presence of Ce^{3+}-mont (106.4 mg) and various amounts of triethylamine at 80 °C for 2 h.



Scheme 2.

(2). The reaction was then applied to a variety of reactants, such as 4-methoxystyrene (**1b**), 4-methylstyrene (**1c**), 4-chlorostyrene (**1d**), *trans*-β-methylstyrene (**1e**), 4-methoxy-*trans*-β-methylstyrene (anethole) (**1f**), α-methylstyrene (**1g**), and 4-chloro-α-methylstyrene (**1h**), in the presence of several effective M^{n+}-monts (Table 3 and Chart 1). In contrast to the case of **1a**, activated styrenes **1b** and **1c** rapidly polymerized in toluene in the presence of Fe^{3+}-, Ce^{3+}-, Al^{3+}-, or Zr^{4+}-mont, and the expected products **5b** and **5c** were obtained in quite low yields only in dioxane. On the other hand, compound **1d** reacted smoothly with **2** (Chart 2) in toluene in the presence of Ce^{3+}-mont to produce **5d** in good yield. β-Methylstyrenes (**1e** and **1f**) and α-methylstyrenes (**1g** and **1h**) reacted smoothly with **2** in dioxane to afford the corresponding 1,3-dioxanes in over 60% yield, but in toluene or benzene as the solvent **1g** gave only the cyclization product **6** in high yield. Although carbonyl ene reactions in the presence of H^+-mont (montmorillonite K10) were known,[12] such reactions did not occur with α- and β-methylstyrenes under our conditions, and, thus, only **5g** was obtained from **1g** and products via an ene reaction, such as 3-phenyl-3-buten-1-ol, were not produced. This supports the assumption that Brønsted acid sites of M^{n+}-monts may act predominantly in this reaction.

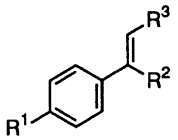
4-Nitrostyrene, allylbenzene, 4-methoxyallylbenzene, 1,1-diphenylethene, 1-octene, *trans*-2-octene, cyclohexene, cyclooctene, and limonene did not react with **2** in toluene at 80 °C in the presence of Ce^{3+}- or Fe^{3+}-mont. 1,1-Diphenylethene rapidly polymerized to unidentified resinous compounds in toluene in the presence of Ce^{3+}- or Fe^{3+}-mont, and even in dioxane in the presence of Zr^{4+}-mont.

Prins Reaction of Styrene (1a) with Aldehydes (3 and 4). A variety of aldehydes, such as 1,3,5-trioxane (**3a**), paraldehyde (**3b**) (Chart 3), acetaldehyde (**4a**), propanal (**4b**), pentanal (**4c**), hexanal (**4d**), and octanal (**4e**) (Chart 4), were used in place of **2** (Table 4). Compound **3a** could be used similarly as **2**, and Ce^{3+}-mont was also regenerated and reused. The reactivity of **3b** was slightly low, and the use of a much M^{n+}-mont was necessary to obtain a high yield of the

Table 3. Prins Reaction of Various Styrene Derivatives with **2**[a]

Run	Styrenes	M^{n+}-Mont			Solvent	Temp	Time	Product	Isolated yield[c]	TON[d]
			mg	(mmol)[b]		°C	h		%	
1	**1b**	Zr^{4+},	68.1	(0.05)	Dioxane	80	1	**5b**	3	3
2	**1c**	Zr^{4+},	68.1	(0.05)	Dioxane	80	1	**5c**	28	2.8×10
3	**1d**	Ce^{3+},	354.6	(0.05)	Toluene	80	6	**5d**	79	7.9×10
4	**1e**	Ce^{3+},	106.4	(0.015)	Dioxane	80	12	**5e**[e]	61	2.0×10^2
5	**1f**	Ce^{3+},	106.4	(0.015)	Dioxane	80	12	**5f**[f]	99	3.3×10^2
6	**1g**	Ce^{3+},	354.6	(0.05)	Dioxane	80	1	**5g**	40	4.0×10
7	**1g**	Zr^{4+},	68.1	(0.05)	Dioxane	80	1	**5g**	37	3.7×10
8	**1h**	Ce^{3+},	354.6	(0.05)	Dioxane	80	1	**5h**	66	6.6×10
9	**1h**	Zr^{4+},	68.1	(0.05)	Dioxane	80	1	**5h**	70	7.0×10
10	**1g**	Ce^{3+},	354.6	(0.05)	Toluene	25	1	**6**	>99	9.9×10

a) Styrenes (5 mmol), **2** (10 mmol), and solvent (10 cm^3). b) The number of acid sites (see Experimental section). c) Based on styrenes. d) Based on the number of acid sites. e) Isomer ratio, *cis* : *trans* = 30 : 70 estimated by ^{1}H NMR. f) Isomer ratio, *cis* : *trans* = 9 : 91 estimated by ^{1}H NMR.



1

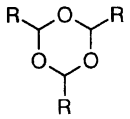
a; R^1 = H, R^2 = H, R^3 = H
b; R^1 = MeO, R^2 = H, R^3 = H
c; R^1 = Me, R^2 = H, R^3 = H
d; R^1 = Cl, R^2 = H, R^3 = H
e; R^1 = H, R^2 = H, R^3 = Me
f; R^1 = MeO, R^2 = H, R^3 = Me
g; R^1 = H, R^2 = Me, R^3 = H
h; R^1 = Cl, R^2 = Me, R^3 = H

Chart 1.

$(CH_2O)_n$

2

Chart 2.



3

a; R = H
b; R = Me

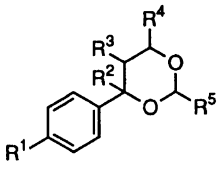
Chart 3.

RCHO

4

a; R = Me
b; R = Et
c; R = Bu
d; R = $CH_3(CH_2)_4$
e; R = $CH_3(CH_2)_6$

Chart 4.



5

a; R^1 = H, R^2 = H, R^3 = H, R^4 = H, R^5 = H
b; R^1 = MeO, R^2 = H, R^3 = H, R^4 = H, R^5 = H
c; R^1 = Me, R^2 = H, R^3 = H, R^4 = H, R^5 = H
d; R^1 = Cl, R^2 = H, R^3 = H, R^4 = H, R^5 = H
e; R^1 = H, R^2 = H, R^3 = Me, R^4 = H, R^5 = H
f; R^1 = MeO, R^2 = H, R^3 = Me, R^4 = H, R^5 = H
g; R^1 = H, R^2 = Me, R^3 = H, R^4 = H, R^5 = H
h; R^1 = Cl, R^2 = Me, R^3 = H, R^4 = H, R^5 = H
i; R^1 = H R^2 = H R^3 = H R^4 = Me, R^5 = Me
j; R^1 = H R^2 = H R^3 = H R^4 = Et, R^5 = Et
k; R^1 = H R^2 = H R^3 = H R^4 = Bu, R^5 = Bu
l; R^1 = H R^2 = H R^3 = H R^4 = $CH_3(CH_2)_4$, R^5 = $CH_3(CH_2)_4$
m; R^1 = H R^2 = H R^3 = H R^4 = $CH_3(CH_2)_6$, R^5 = $CH_3(CH_2)_6$
n; R^1 = H R^2 = H R^3 = H R^4 = H, R^5 = Me

Chart 5.

corresponding 1,3-dioxanes. Although the reactivity of the aldehydes (**4a**—**4e**) was also low, the corresponding products (**5i**—**5m**) (Chart 5) were obtained by using a larger amount of Fe^{3+}-mont and a longer time. In these cases, the oligomers of **4a**, **4b**, **4c**, **4d**, and **4e** were sometimes produced.

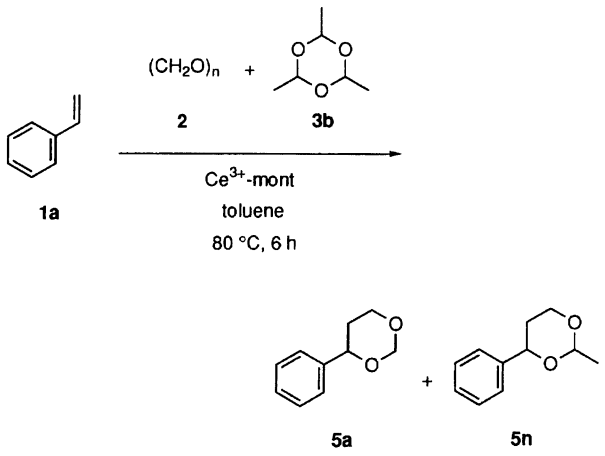
Compound **1a** did not react at all with benzaldehyde in toluene in the presence of Ce^{3+}- or Fe^{3+}-mont at 80 °C for 24 h. Tetradecanal, 2,2-dimethylpropanal, and 30% formalin did not react with **1a** in the presence of Fe^{3+}-mont at 80 °C for 24 h, probably because of the shape-selectivity due to the layer structure, the deactivation of catalysts by a large excess of water molecules, or any other reasons.

Competitive Prins Reaction of Styrene (1a) with Mixed Aldehydes. A similar treatment of **1a** with a mixture of **2** (2 equiv to **1a**) and **3b** (2 equiv to **1a**) in toluene in the presence of Ce^{3+}-mont at 80 °C for 6 h afforded **5a** in 69% yield and **5n** in 19% yield, respectively (Scheme 3). Under these conditions **5i**, which could be derived from the

Table 4. Prins Reaction of **1a** with Various Trioxanes and Aldehydes[a)]

Run	Trioxane or aldehyde	M^{n+}-Mont			Time	Product	Isolated yield[c)]	TON[d)]
		mg	(mmol)[b)]		h		%	
1	**3a**	Ce^{3+}, 354.6	(0.05)	1st	6	**5a**	90	9.0×10
2	**3a**	Ce^{3+}, 354.6	(0.05)	2nd	6	**5a**	89	8.9×10
3	**3a**	Ce^{3+}, 354.6	(0.05)	3rd	6	**5a**	88	8.8×10
4	**3b**	Ce^{3+}, 354.6	(0.05)		6	**5i**	34	3.4×10
5	**3b**	Fe^{3+}, 716.3	(0.25)		12	**5i**	87	1.7×10
6	**4a**	Fe^{3+}, 716.3	(0.25)		12	**5i**	65	1.3×10
7	**4b**	Fe^{3+}, 716.3	(0.25)		12	**5j**	44	9
8	**4c**	Fe^{3+}, 716.3	(0.25)		12	**5k**	47	9
9	**4d**	Fe^{3+}, 716.3	(0.25)		12	**5l**	27	5
10	**4e**	Fe^{3+}, 716.3	(0.25)		12	**5m**	29	6

a) **1a** (5 mmol), trioxane or aldehyde (10 mmol), and toluene (10 cm^3) at 80 °C. b) The number of acid sites (see Experimental section). c) Based on **1a**. d) Based on the number of acid sites.



Scheme 3.

reaction of **1a** with **3b**, was not produced at all. Compound **5n** might be produced via either the reaction of **3b** with the intermediary carbocation produced from **1a** and formaldehyde or the transacetalization of **5a** with acetaldehyde or **3b**. On the other hand, a similar competitive reaction of **1a** with a mixture of **2** and benzaldehyde afforded only **5a** in 90% yield. 2,4,6-Triphenyl-1,3-dioxane or 2,4-diphenyl-1,3-dioxane, which can be derived from benzaldehyde, was not produced at all. The reaction of **1a** with a mixture of **3b** and benzaldehyde afforded **5i** selectively in 69% yield. These results may reflect a difference in the electrophilic ability of each aldehyde or trioxane to **1a** and/or the shape-selectivity (a larger benzaldehyde did not react) derived from the interlayer structure of Ce^{3+}-mont.

Conclusion

The M^{n+}-mont-catalyzed facile Prins reaction was developed. Thus, the reaction of styrene (**1a**) with paraformaldehyde (**2**) in toluene in the presence of Ce^{3+}- or Fe^{3+}-mont gave 4-phenyl-1,3-dioxane (**5a**) selectively in up to 90% isolated yield with a turnover number of up to 5.9×10^2 and in up to 93% with 5.8×10^2, respectively. The regeneration and recycling of M^{n+}-mont were confirmed with Ce^{3+}-mont. The catalytic efficiency of M^{n+}-monts was roughly in the following order: Ce^{3+}-, Fe^{3+}-> Dy^{3+}-> H^+-$\gg Al^{3+}$-, La^{3+}-, Pr^{3+}-, Nd^{3+}-, Eu^{3+}-> Tb^{3+}-, Ho^{3+}-, Gd^{3+}-, Mg^{2+}-, Zr^{4+}-, Zn^{2+}-, Ca^{2+}-, Y^{3+}-, Sm^{3+}-> Er^{3+}-, Yb^{3+}-> Na^+-mont.

Experimental

NMR spectra were recorded on JEOL EX-400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) and JEOL GSX-270 (^{1}H NMR, 270 MHz; ^{13}C NMR, 67.8 MHz) instruments for solutions in $CDCl_3$ with $(CH_3)_4Si$ as an internal standard. The coupling constants (J) are given in Hz. Some abbreviations are listed as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; a, axial; e, equatorial. Mass spectra were measured on a Shimadzu QP-5000S mass spectrometer equipped with a Shimadzu GC-17 gas-liquid chromatography (30 m×0.254 mm, 0.25 μm film thickness, J&W Scientific fused silica capillary column DB-1) with electron-impact method for ionization (ionizing voltage, 70 eV). GLC analyses were performed 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 flame-ionization detectors and helium as carrier gas. The melting points were determined on a Yanaco MP-S3 micro melting point apparatus and uncorrected. X-Ray powder diffraction (XRD) data were obtained on a Shimadzu XD-D1 diffractometer using Cu $K\alpha$ radiation and an energy dispersive detector. X-Ray fluorescence (XRF) analyses were carried out at the Environment Preservation Center of Kyoto University. Combustion analyses were performed at the Microanalytical Center of Kyoto University.

Commercially available organic compounds, except for **2**, **3a**, **3b**, and **4a**, were purified by a known method before use.[13] Commercially available inorganic compounds were used without further purification. Kunipia® G, namely Na^+-mont, was obtained from Kunimine Industries Co., Ltd. Montmorillonite K10, namely H^+-mont, was commercially available from Aldrich Chemical Co., Inc., which was used as obtained. M^{n+}-monts ($M^{n+}=Ce^{3+}$, Fe^{3+}, Al^{3+}, Zr^{4+}, Zn^{2+}, Mg^{2+}, Ca^{2+})[14] were prepared from Na^+-mont [Kunipia® G: approximate formula, $Na_{0.33}Al_{1.67}Mg_{0.33}(Si_4O_{10})(OH)_2\cdot nH_2O$; cation exchanging capacity 1.15 mequiv g^{-1}] as described before.[3a,3b] The range of the isolated yield of M^{n+}-monts ($M^{n+}=Ce^{3+}$, Al^{3+}, Zr^{4+}, Zn^{2+}, Mg^{2+}, Ca^{2+}) was 83 to 100 wt% based on Na^+-mont, while Fe^{3+}-mont was reproducibly obtained in 113 wt% yield, which might contain an excess iron species other than iron(III) nitrate. Ln^{3+}-monts[15] such as Y^{3+}-, La^{3+}-, Pr^{3+}-, Nd^{3+}-, Dy^{3+}-, Sm^{3+}-, Eu^{3+}-, Gd^{3+}-, Tb^{3+}-, Ho^{3+}-, Er^{3+}-, and Yb^{3+}-monts were prepared similarly in one-sixth scale using $Y(NO_3)_3\cdot6H_2O$, $La(NO_3)_3\cdot6H_2O$, $Pr(NO_3)_3\cdot nH_2O$ (used as $n=4$), $Nd(NO_3)_3\cdot6H_2O$, $Dy(NO_3)_3\cdot6H_2O$, $Sm(NO_3)_3\cdot6H_2O$, $EuCl_3\cdot6H_2O$, $Gd(NO_3)_3\cdot6H_2O$, $TbCl_3\cdot6H_2O$, $Ho(NO_3)_3\cdot nH_2O$ (used as $n=3$), $Er(NO_3)_3\cdot6H_2O$, and $Yb(NO_3)_3\cdot4H_2O$ in 45 to 88 wt% isolated yield, respectively.[3a,16] The color of freshly prepared Ln^{3+}-monts was white. The amount of acid sites (Brønsted and Lewis acid sites) of Y^{3+}-, La^{3+}-, Ce^{3+}-, Pr^{3+}-, Nd^{3+}-, Sm^{3+}-, Eu^{3+}-, Gd^{3+}-, Tb^{3+}-, Dy^{3+}-, Ho^{3+}-, Er^{3+}-, and Yb^{3+}-monts was estimated by NH_3-TPD analyses to be 0.315, 0.200, 0.141, 0.140, 0.125, 0.275, 0.109, 0.250, 0.204, 0.059, 0.216, 0.266, and 0.323 mmol g^{-1}, respectively, at 100 °C.[3a] The basal spacings (d_{001}) of Y^{3+}-, La^{3+}-, Ce^{3+}-, Pr^{3+}-, Nd^{3+}-, Sm^{3+}-, Eu^{3+}-, Gd^{3+}-, Tb^{3+}-, Dy^{3+}-, Ho^{3+}-, Er^{3+}-, and Yb^{3+}-monts were clarified by a sharp peak obtained on XRD analyses to be 15.1, 15.2, 15.2, 15.0, 14.8, 15.0, 14.9, 14.4, 14.4, 14.5, 14.9, 14.9, and 14.9 Å, respectively, which indicated that all of the monts have a layer structure. All of the products were isolated by column chromatography and characterized by their spectral data and/or melting point as well as C and H combustion analyses: **5a**,[17] **5b**,[18] **5c**,[18,19] **5d**,[8a,18] **5e**,[8a,20] **5f**,[8a] **5g**,[21] **5i**,[22] **5j**,[22] **5n**,[23] and **6**[24—26] are known compounds, while **5h**, **5k**, **5l**, and **5m** are new.

General Procedure for Prins Reaction and Product Isolation. The Prins reaction of **1a** with **2** in the presence of Ce^{3+}-mont is described below (Table 2, Run 8). To a mixture of **1a** (520.8 mg, 5.0 mmol), dry toluene (10 cm^3), and **2** (300.4 mg, 10.0 mmol) was added Ce^{3+}-mont (354.6 mg, 0.05 mmol as acid sites) at 25 °C. The mixture was stirred with a magnetic stirrer at 80 °C for 6 h. After the mixture had been cooled, the catalyst was filtered with suction (Toyo, quantitative filter paper No. 4A) to recover and rinsed with diethyl ether (10 cm^3). The solvent in a mixture of the filtrate and the ethereal washings was removed under reduced pressure to leave a colorless oil, which was subjected to a silica-gel column chromatography (Wakogel® C-300; eluents, hexane and then hexane : ethyl acetate = 95 : 5). After concentration of the fractions, a colorless oil of **5a** was obtained (739.3 mg, 4.50 mmol, 90% isolated yield), which was identified by ^{13}C NMR;[27] ^{1}H NMR

(400 MHz) δ = 1.69—1.75 (1H, m, 5-H), 2.04—2.16 (1H, m, 5-H), 3.83—3.92 (1H, m, 6-H), 4.17—4.24 (1H, m, 6-H), 4.65 (1H, dd, J = 11.2, 2.4 Hz, 4-H_a), 4.90 (1H, d, J = 6.4 Hz, 2-H), 5.22 (1H, d, J = 6.4 Hz, 2-H), 7.24—7.40 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 33.9 (t), 66.9 (t), 78.7 (d), 94.2 (t), 125.8 (d, 2×C), 127.8 (d), 128.5 (d, 2×C), 141.4 (s); MS *m/z* 164 (M^+; 4%), 118 (62), 105 (100), 77 (40). Found: C, 73.04; H, 7.35%. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. The recovered Ce^{3+}-mont was regenerated by washing with 50% aqueous acetone (10 cm^3) with a magnetic stirring at room temperature for 24 h followed by filtering and drying at 120 °C in an electric oven for 24 h.

4-(4-Methoxyphenyl)-1,3-dioxane (5b). A colorless needle-like crystal; mp 70.5—71.0 °C (lit,[18] 70—72 °C); ^{1}H NMR (400 MHz) δ = 1.64—1.71 (1H, m, 5-H), 2.04—2.17 (1H, m, 5-H), 3.80 (3H, s, CH_3O), 3.82—3.90 (1H, m, 6-H), 4.16—4.23 (1H, m, 6-H), 4.59 (1H, dd, J = 11.2, 2.4 Hz, 4-H_a), 4.88 (1H, d, J = 6.4 Hz, 2-H), 5.19 (1H, d, J = 6.4 Hz, 2-H), 6.89 (2H, d, J = 8.8 Hz, ArH, AA′XX′ type), 7.30 (2H, d, J = 8.8 Hz, ArH, AA′XX′ type); ^{13}C NMR (100 MHz) δ = 33.9 (t), 55.3 (q), 67.0 (t), 78.5 (d), 94.2 (t), 113.9 (d, 2×C), 127.2 (d, 2×C), 133.7 (s), 159.3 (s); MS *m/z* 194 (M^+; 21%), 136 (100). Found: C, 67.80; H, 7.24%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%.

4-(4-Methylphenyl)-1,3-dioxane (5c). A colorless oil; ^{1}H NMR (400 MHz) δ = 1.61—1.68 (1H, m, 5-H), 2.00—2.12 (1H, m, 5-H), 2.32 (3H, s, CH_3), 3.77—3.86 (1H, m, 6-H), 4.12—4.18 (1H, m, 6-H), 4.57 (1H, dd, J = 11.2, 2.5 Hz, 4-H_a), 4.85 (1H, d, J = 6.4 Hz, 2-H), 5.18 (1H, d, J = 6.4 Hz, 2-H), 7.14 (2H, d, J = 7.8 Hz, ArH, AA′BB′ type), 7.24 (2H, d, J = 7.8 Hz, ArH, AA′BB′ type); ^{13}C NMR (100 MHz) δ = 21.1 (q), 33.9 (t), 66.9 (t), 78.6 (d), 94.1 (t), 125.7 (d, 2×C), 129.1 (d, 2×C), 137.4 (s), 138.6 (s); MS *m/z* 178 (M^+; 7%), 132 (33), 119 (100), 91 (29). Found: C, 74.25; H, 7.88%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

4-(4-Chlorophenyl)-1,3-dioxane (5d). A colorless oil; ^{1}H NMR (400 MHz) δ = 1.64—1.69 (1H, m, 5-H), 1.94—2.06 (1H, m, 5-H), 3.79—3.86 (1H, m, 6-H), 4.14—4.19 (1H, m, 6-H), 4.59 (1H, dd, J = 11.2, 2.4 Hz, 4-H_a), 4.85 (1H, d, J = 6.4 Hz, 2-H), 5.19 (1H, d, J = 6.4 Hz, 2-H), 7.28 (2H, d, J = 8.8 Hz, ArH, AA′BB′ type), 7.30 (2H, d, J = 8.8 Hz, ArH, AA′BB′ type); ^{13}C NMR (100 MHz) δ = 33.9 (t), 66.7 (t), 77.8 (d), 94.1 (t), 127.1 (d, 2×C), 128.6 (d, 2×C), 133.4 (s), 140.1 (s); MS *m/z* 198 (M^+; 14%), 139 (100). Found: C, 60.54; H, 5.65%. Calcd for $C_{10}H_{11}ClO_2$: C, 60.49; H, 5.58%.

5-Methyl-4-phenyl-1,3-dioxane (5e). A colorless oil; *cis* : *trans* = 30 : 70. *cis*-Isomer identified by ^{1}H NMR;[20] ^{1}H NMR (400 MHz) δ = 0.91 (3H, d, J = 7.3 Hz, 5-CH_3), 1.85 (1H, m, 5-H_e), 3.93 (1H, d, J = 11.2 Hz, 6-H), 4.05 (1H, dd, J = 11.2, 2.4 Hz, 6-H), 4.87 (1H, d, J = 2.4 Hz, 4-H_a), 4.89 (1H, d, J = 6.4 Hz, 2-H), 5.24 (1H, d, J = 6.4 Hz, 2-H), 7.18—7.39 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 11.1 (q), 34.9 (d), 73.1 (t), 80.6 (d), 94.6 (t), 125.1 (d, 2×C), 127.0 (d), 128.2 (d, 2×C), 140.5 (s); MS *m/z* 178 (M^+; 1%), 107 (100): *trans*-isomer identified by ^{1}H NMR;[20] ^{1}H NMR (400 MHz) δ = 0.59 (3H, d, J = 6.8 Hz, 5-CH_3), 2.07—2.13 (1H, m, 5-H_a), 3.41 (1H, t, J = 11.2 Hz, 6-H_e), 4.10 (1H, dd, J = 11.2, 4.9 Hz, 6-H_a), 4.11 (1H, d, J = 10.3 Hz, 4-H_a), 4.83 (1H, d, J = 6.4 Hz, 2-H), 5.20 (1H, d, J = 6.4 Hz, 2-H), 7.18—7.39 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 12.5 (q), 36.4 (d), 73.0 (t), 86.2 (d), 94.1 (t), 127.4 (d, 2×C), 128.3 (d), 128.4 (d, 2×C), 139.5 (s); MS *m/z* 178 (M^+; 1%), 107 (100). Found: C, 74.41; H, 7.76% as a mixture of isomers. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

4-(4-Methoxyphenyl)-5-methyl-1,3-dioxane (5f). A colorless oil; *cis* : *trans* = 9 : 91; the spectral data of the major *trans*-isomer are as follows; ^{1}H NMR (400 MHz) δ = 0.54 (3H, d, J = 6.8 Hz, CH_3), 1.98—2.15 (1H, m, 5-H_e), 3.35 (1H, t, J = 11.2 Hz, 6-H_e), 3.74 (3H, s, CH_3O), 4.03 (1H, d, J = 10.3 Hz, 4-H_a), 4.07 (1H, dd, J = 11.2, 4.4 Hz, 6-H_a), 4.78 (1H, d, J = 6.3 Hz, 2-H), 5.15 (1H, d, J = 6.3 Hz, 2-H), 6.87 (2H, d, J = 8.8 Hz, ArH, AA′XX′ type), 7.27 (2H, d, J = 8.8 Hz, ArH, AA′XX′ type); ^{13}C NMR (100 MHz) δ = 12.5 (q), 36.4 (d), 55.1 (q), 72.9 (t), 85.6 (d), 94.1 (t), 113.7 (d, 2×C), 128.5 (d, 2×C), 131.8 (s), 159.5 (s); MS *m/z* 208 (M^+; 18%), 136 (100). Found: C, 69.20; H, 8.04%. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

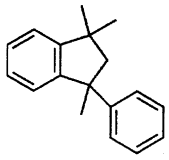
4-Methyl-4-phenyl-1,3-dioxane (5g). A colorless oil; ^{1}H NMR (400 MHz) δ = 1.46 (3H, s, CH_3), 2.10—2.19 (1H, m, 5-H), 2.25—2.32 (1H, m, 5-H), 3.65—3.73 (1H, m, 6-H), 3.90—3.97 (1H, m, 6-H), 4.73 (1H, d, J = 6.4 Hz, 2-H), 4.91 (1H, d, J = 6.4 Hz, 2-H), 7.23—7.31 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 32.1 (q), 34.9 (t), 63.6 (t), 75.7 (s), 89.1 (t), 125.7 (d, 2×C), 127.0 (d), 128.7 (d, 2×C), 144.1 (s); MS *m/z* 178 (M^+; < 0.1%), 163 (30), 132 (41), 117 (40), 105 (100), 91 (47), 77 (44), 51 (37). Found: C, 74.21; H, 7.98%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

4-(4-Chlorophenyl)-4-methyl-1,3-dioxane (5h). A colorless oil; ^{1}H NMR (400 MHz) δ = 1.46 (3H, s, CH_3), 2.09—2.17 (1H, m, 5-H), 2.20—2.26 (1H, m, 5-H), 3.64—3.71 (1H, m, 6-H), 3.91—3.98 (1H, m, 6-H), 4.71 (1H, d, J = 6.3 Hz, 2-H), 4.92 (1H, d, J = 6.3 Hz, 2-H), 7.32 (2H, d, J = 8.8 Hz, ArH, AA′BB′ type), 7.35 (2H, d, J = 8.8 Hz, ArH, AA′BB′ type); ^{13}C NMR (100 MHz) δ = 31.6 (q), 34.9 (t), 63.5 (t), 75.3 (s), 89.1 (t), 127.2 (d, 2×C), 128.9 (d, 2×C), 132.9 (s), 142.9 (s); MS *m/z* 212 (M^+; 3%), 197 (36), 167 (19), 139 (100), 125 (18), 111 (16), 75 (20), 51 (18). Found: C, 62.34; H, 6.09%. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16%.

2,*c*-6-Dimethyl-*c*-4-phenyl-1,3-dioxane (5i). A colorless oil; the stereochemistry of 2-hydrogen was assigned to be *axial* by considering the report of Gaset et al.[8b] in which 2-, 4-, 6-hydrogens of 2,4,6-trisubstituted 1,3-dioxanes are situated on *axial* positions and also by comparing its chemical shift with the calculated shifts (δ = 4.94 and δ = 5.26 for *axial* and *equatorial* hydrogen, respectively;[28,29] ^{1}H NMR (400 MHz) δ = 1.27 (3H, d, J = 5.9 Hz, 6-CH_3), 1.43 (3H, d, J = 5.0 Hz, 2-CH_3), 1.57 (1H, ddd, J = 12.9, 11.4, 10.9 Hz, 5-H_a), 1.74 (1H, ddd, J = 12.9, 3.0, 2.5 Hz, 5-H_e), 3.89 (1H, dqd, J = 10.9, 5.9, 2.5 Hz, 6-H_a), 4.65 (1H, dd, J = 11.4, 3.0 Hz, 4-H_a), 4.91 (1H, q, J = 5.0 Hz, 2-H_a), 7.15—7.39 (5H, m, ArH); ^{13}C NMR (67.8 MHz) δ = 21.3 (q), 21.6 (q), 40.4 (t), 72.5 (d), 78.4 (d), 98.8 (d), 125.9 (d, 2×C), 127.7 (d), 128.4 (d, 2×C), 141.7 (s); MS *m/z* 192 (M^+; 0.6%), 148 (30), 131 (39), 107 (100), 77 (33), 45 (74). Found: C, 75.10; H, 8.45%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

2,*c*-6-Diethyl-*c*-4-phenyl-1,3-dioxane (5j). A colorless oil; the stereochemistry was assumed to be the same as that of **5i**; ^{1}H NMR (270 MHz) δ = 0.96 (3H, t, J = 7.4 Hz, CH_3), 0.99 (3H, t, J = 7.4 Hz, CH_3), 1.44—1.82 (6H, m, 3×CH_2), 3.64 (1H, m, 6-H_a), 4.64 (1H, dd, J = 11.4, 2.0 Hz, 4-H_a), 4.66 (1H, t, J = 5.2 Hz, 2-H_a), 7.10—7.40 (5H, m, ArH); ^{13}C NMR (67.8 MHz) δ = 8.5 (q), 9.5 (q), 28.2 (t), 28.8 (t), 38.8 (t), 77.8 (d), 78.3 (d), 102.9 (d), 125.8 (d, 2×C), 127.5 (d), 128.4 (d, 2×C), 142.1 (s); MS *m/z* 220 (M^+; < 0.1%), 191 (16), 145 (68), 107 (93), 77 (27), 56 (100), 41 (48). Found: C, 76.63; H, 9.05%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

2,*c*-6-Dibutyl-*c*-4-phenyl-1,3-dioxane (5k). A colorless oil; the stereochemistry was assumed to be the same as that of **5i**; ^{1}H NMR (400 MHz) δ = 0.91 (6H, t, J = 7.1 Hz, 2×CH_3), 1.32—1.78 (14H, m, 7×CH_2), 3.70 (1H, m, 6-H_a), 4.63 (1H, dd, J = 11.2, 2.4 Hz, 4-H_a), 4.71 (1H, t, J = 5.4 Hz, 2-H_a), 7.23—7.38 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 14.0 (q, 2×C), 22.6 (t), 22.7 (t), 26.4 (t), 27.2 (t), 34.9 (t), 35.6 (t), 39.3 (t), 76.6 (d), 78.3 (d), 102.1 (d), 125.8 (d, 2×C), 127.5 (d), 128.4 (d, 2×C), 142.1 (s); MS *m/z*



6

Chart 6.

276 (M^+; < 0.1%), 219 (14), 173 (45), 117 (32), 107 (100), 84 (21), 69 (32), 56 (34), 41 (82). Found: C, 78.30; H, 10.22%. Calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21%.

2,*c*-6-Dipentyl-*c*-4-phenyl-1,3-dioxane (5l). A colorless oil; the stereochemistry was assumed to be the same as that of **5i**; ^{1}H NMR (400 MHz) δ = 0.89 (6H, t, J = 6.6 Hz, 2×CH_3), 1.20—1.80 (18H, m, 9×CH_2), 3.70 (1H, m, 6-H_a), 4.64 (1H, dd, J = 11.2, 2.4 Hz, 4-H_a), 4.71 (1H, t, J = 5.1 Hz, 2-H_a), 7.20—7.40 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 14.0 (q, 2×C), 22.6 (t, 2×C), 23.9 (t), 24.7 (t), 31.7 (t), 31.8 (t), 35.1 (t), 35.9 (t), 39.3 (t), 76.6 (d), 78.3 (d), 102.1 (d), 125.8 (d, 2×C), 127.5 (d), 128.4 (d, 2×C), 142.1 (s); MS *m/z* 304 (M^+; < 0.1%), 233 (16), 187 (52), 117 (36), 107 (100), 91 (24), 55 (74), 41 (50). Found: C, 79.20; H, 10.29%. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59%.

2,*c*-6-Diheptyl-*c*-4-phenyl-1,3-dioxane (5m). A colorless oil; the stereochemistry was assumed to be the same as that of **5i**; ^{1}H NMR (400 MHz) δ = 0.87 (6H, t, J = 6.8 Hz, 2×CH_3), 1.20—1.80 (26H, m, 13×CH_2), 3.70 (1H, m, 6-H_a), 4.63 (1H, dd, J = 11.2, 2.0 Hz, 4-H_a), 4.70 (1H, t, J = 5.1 Hz, 2-H_a), 7.20—7.40 (5H, m, ArH); ^{13}C NMR (100 MHz) δ = 14.1 (q, 2×C), 22.7 (t, 2×C), 24.3 (t), 25.1 (t), 29.3 (t, 2×C), 29.5 (t), 29.6 (t), 31.8 (t, 2×C), 35.1 (t), 35.9 (t), 39.3 (t), 76.6 (d), 78.3 (d), 102.1 (d), 125.8 (d, 2×C), 127.5 (d), 128.4 (d, 2×C), 142.1 (s); MS *m/z* 360 (M^+; < 0.1%), 261 (9), 215 (65), 117 (28), 107 (100), 91 (27), 69 (31), 55 (51), 43 (62). Found: C, 80.23; H, 11.16%. Calcd for $C_{24}H_{40}O_2$: C, 79.94; H, 11.18%.

***cis*-2-Methyl-4-phenyl-1,3-dioxane (5n).** A colorless oil which was identified by ^{1}H NMR,[23] ^{13}C NMR,[23] and mass spectra as a mixture with **5a** (**5a** : **5n** = 2 : 1); MS *m/z* 178 (M^+; 2%), 134 (26), 117 (75), 105 (100), 77 (49), 72 (62), 51 (43).

1,1,3-Trimethyl-3-phenylindan (6). A white leaf-like crystal which was identified by ^{1}H NMR,[24,25] ^{13}C NMR,[24] mass spectrum,[24] and mp;[25,26] mp 51.5—52.5 °C (lit, 53.5—54.0 °C[25] and 52 °C[26]) (Chart 6). Found: C, 91.43; H, 8.42%. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53%.

Trial for Estimation of the Number of Active Acid Sites on Ce^{3+}-Mont with Triethylamine-Doped Toluene. By following a literature method,[3d,3e,10] a mixture of freshly-prepared triethylamine-doped toluene (10.0 cm^3; it contains various amounts of Et_3N) and Ce^{3+}-mont (106.4 mg) was stirred magnetically at 25 °C for 2 h. To the mixture were added the freshly distilled **1a** (520.8 mg, 5.00 mmol) and **2** (300.4 mg, 10.0 mmol). The mixture was stirred at 25 °C for 5 min and then stirred at 80 °C. After it had been cooled, the reaction mixture was filtered by suction. The catalyst was rinsed with diethyl ether (5 cm^3). Acetophenone was added to a mixture of the filtrate and the washing as an internal standard. Both unreacted **5a** and the recovered **1a** were estimated by GLC.

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