

Metal cation-exchanged montmorillonite (M^{n+} -Mont)-catalysed carbonyl-ene reactions

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Jun-ichi Tateiwa, Akihiro Kimura, Masaaki Takasuka and Sakae Uemura^{*†}

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Metal cation-exchanged montmorillonite (M^{n+} -mont) works in acetonitrile at 80 °C as a Lewis acid catalyst for the intermolecular carbonyl-ene reaction of α -methylstyrenes with paraformaldehyde to give the corresponding homoallylic alcohols, Zr^{4+} -mont being the most effective of the many M^{n+} -mont catalysts examined. Similarly, the catalyst is also useful for the highly stereoselective intramolecular cyclization of citronellals to afford isopulegols, the reaction being much faster. Regeneration of the catalyst is confirmed for Zr^{4+} -mont, which can be effectively recycled at least five times.

Introduction

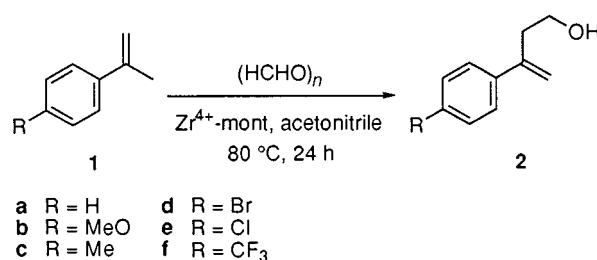
Currently, we have been much involved in the use of cation-exchanged montmorillonites (M^{n+} -mont) as heterogeneous clay catalysts in organic synthesis, the hope being to improve the selectivity of the reactions and also to make the reaction sequences environmentally friendly.^{1,2}

We recently reported the M^{n+} -mont-catalysed Prins reaction between alkenes and several aldehydes to give 1,3-dioxane derivatives selectively, where the clay functioned as a Brønsted acid catalyst.³ During the course of this study we came across a closely related reaction, the so-called carbonyl-ene reaction, which affords homoallylic alcohols when the solvent used is changed from toluene, benzene and 1,4-dioxane to acetonitrile which has greater coordinating ability; here the clay functioned as a Lewis acid catalyst. Application of this reaction to 3,7-dimethyloct-6-enal (citronellal) resulted in an intramolecular cyclization to provide 2-isopropenyl-5-methylcyclohexanol (isopulegol) highly stereoselectively. We report here our results for these M^{n+} -mont catalysed ene reactions. It is worth noting that clay K-10 (H_2SO_4 -treated montmorillonite) has been shown to work as a catalyst for similar reactions: namely, the reaction between alkenes and diethyl oxomalonate to give γ -lactones⁴ and the cyclization of citronellal to isopulegol and neoisopulegol.⁵

Results and discussion

Intermolecular carbonyl-ene reaction between α -methylstyrenes and paraformaldehyde in the presence of M^{n+} -mont

Treatment of α -methylstyrene **1a** with paraformaldehyde (2 mol equiv.) in acetonitrile in the presence of Zr^{4+} -mont (5 mol%, 58 wt%) at 80 °C for 24 h produced 3-phenylbut-3-en-1-ol **2a** in 61% isolated yield (Scheme 1; Table 1, run 1, 80% yield based on **2a** consumed). The turnover number was calculated as 11.7 based on the amount of acid sites of Zr^{4+} -mont estimated by the temperature-programmed desorption of ammonia gas (NH_3 -TPD) method.⁶ Lengthening the reaction time failed to improve the product yield. At higher temperatures the reaction was accompanied by the unwanted formation of polymeric products, while at 25 °C it failed to proceed. There was little reaction in tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) (runs 6–9). Further reaction of the resulting compound **2a** with additional paraformaldehyde did not



Scheme 1

occur whilst we separately confirmed that **2a** failed to react at all with paraformaldehyde under similar conditions. 4-Methyl-4-phenyl-1,3-dioxane, the product from a Prins reaction in toluene or 1,4-dioxane as solvent,³ was not produced at all under the present conditions.

The recovered Zr^{4+} -mont was successively regenerated and re-used at least 5 times after being washed with 50% aqueous acetone and then dried at 120 °C (runs 1–5).

Fe^{3+} - and Al^{3+} -monts were also shown to be effective for this reaction (runs 11 and 12), but the catalytic activity of other M^{n+} -monts such as Ce^{3+} - and Zn^{2+} -monts was lower (runs 13 and 14). On the other hand, H^+ -mont (commercially available montmorillonite K10) and Na^+ -mont (commercially available Kunipia[®] G) failed to show any catalytic activity (runs 15 and 16). Certainly, the reaction did not proceed without M^{n+} -mont (run 17). Thus, the order of the efficiency of M^{n+} -mont as catalyst was roughly estimated as follows from the product yield: Zr^{4+} -, Fe^{3+} -, Al^{3+} - > Ce^{3+} -, Zn^{2+} - >> H^+ -, Na^+ -mont. The order of the catalytic efficiency of M^{n+} -mont was also estimated as follows from the product yield per weight of the catalyst: Zr^{4+} - > Al^{3+} -, Fe^{3+} - > Zn^{2+} -, Ce^{3+} - >> H^+ -, Na^+ -mont. In this estimation Zr^{4+} -mont was again more effective than other M^{n+} -monts.

The reaction was then applied to substituted α -methylstyrenes, such as *p*-methoxy- α -methylstyrene **1b**, *p*-methyl- α -methylstyrene **1c**, *p*-bromo- α -methylstyrene **1d**, *p*-chloro- α -methylstyrene **1e** and *p*-trifluoromethyl- α -methylstyrene **1f**. Almost all of compound **1b** was consumed to form unidentified polymeric compounds, the expected 3-(4-methoxyphenyl)but-3-en-1-ol **2b** being produced only in a very low yield (run 18). Compounds **1c**, **1d** and **1e** reacted smoothly with paraformaldehyde to produce 3-(4-methylphenyl)but-3-en-1-ol **2c**, 3-(4-bromophenyl)but-3-en-1-ol **2d** and 3-(4-chlorophenyl)but-3-en-1-ol **2e** in fair to good yields (over 80% yield based on alkenes consumed), respectively (runs 19–21). The formation of a little of the formate of the product alcohol (ROCHO; <10%

[†] E-Mail: uemura@scl.kyoto-u.ac.jp

Table 1 Metal cation-exchanged montmorillonite(Mⁿ⁺-mont)-catalysed carbonyl-ene reaction of α -methylstyrenes with paraformaldehyde*

Run	α -Methylstyrenes	M ⁿ⁺ -mont	(w/mg)	Solvent	Product	Yield (%) ^a
1	1a	Zr ⁴⁺	(340.6)	MeCN	2a	47 [61] ^b
2	1a	Zr ⁴⁺ (2nd)	(340.6)	MeCN	2a	43 [56]
3	1a	Zr ⁴⁺ (3rd)	(340.6)	MeCN	2a	32
4	1a	Zr ⁴⁺ (4th)	(340.6)	MeCN	2a	25
5	1a	Zr ⁴⁺ (5th)	(340.6)	MeCN	2a	25
6	1a	Zr ⁴⁺	(340.6)	THF	2a	2
7	1a	Zr ⁴⁺	(340.6)	DMA	2a	1
8	1a	Zr ⁴⁺	(340.6)	DMSO	—	0
9	1a	Zr ⁴⁺	(340.6)	DMF	—	0
10 ^c	1a	Zr ⁴⁺	(340.6)	MeCN	2a	24
11	1a	Fe ³⁺	(716.3)	MeCN	2a	46
12	1a	Al ³⁺	(470.8)	MeCN	2a	31
13	1a	Ce ³⁺	(1773.0)	MeCN	2a	16
14	1a	Zn ²⁺	(673.9)	MeCN	2a	13
15	1a	H ⁺ (K10)	(788.6)	MeCN	2a	1
16	1a	Na ⁺	(500.0)	MeCN	—	0
17	1a	—	—	MeCN	—	0
18	1b	Zr ⁴⁺	(340.6)	MeCN	2b	2
19	1c	Zr ⁴⁺	(340.6)	MeCN	2c	56 [76] ^d
20	1d	Zr ⁴⁺	(340.6)	MeCN	2d	28
21	1e	Zr ⁴⁺	(340.6)	MeCN	2e	25 [54] ^e
22	1e	Fe ³⁺	(716.3)	MeCN	2e	6
23	1f	Zr ⁴⁺	(340.6)	MeCN	2f	4

* Reagents and conditions: α -Methylstyrenes **1** (5 mmol), paraformaldehyde (10 mmol) and Mⁿ⁺-mont (0.25 mmol as acid sites estimated by NH₃-TPD analysis) in solvent (10 cm³) at 80 °C for 24 h. ^a Yield of an isolated pure compound, based on **1**. Crude isolated yield is in [] brackets. ^b 80% Yield based on alkene conversion (76%). ^c Paraformaldehyde (5 mmol). ^d 87% Yield based on alkene conversion (87%). ^e 96% Yield based on alkene conversion (56%)

of the alcohol) was always confirmed by ¹H NMR spectroscopy. On the other hand, compound **1f** scarcely reacted with paraformaldehyde to form 3-(4-trifluoromethylphenyl)but-3-en-1-ol **2f**, nearly all of **1f** being recovered (run 23). Unfortunately, alkenes such as β -methylstyrene, 2,5-dimethylhexa-2,4-diene, hepta-1,6-diene, dec-1-ene and dodec-1-ene failed to react with paraformaldehyde, in each case almost all of the alkene being recovered.

In contrast to the Prins reaction under similar conditions,³ the carbonyl compound which can be employed in this ene reaction is limited to paraformaldehyde and, thus, the reaction of α -methylstyrene with 1,3,5-trioxane, acetaldehyde, metaldehyde and paraldehyde failed to occur, almost all of the alkene being recovered. When chloral (Cl₃CCHO) was used, the reaction resulted in a formation of an isomeric mixture of four α -methylstyrene dimers (all had MW 236 by GC-MS) in 60–70% yield (1,1,3-trimethyl-3-phenylindane;³ 2,4-diphenyl-4-methylpent-2-ene and small amounts of two uncharacterizable compounds) without any ene-reaction products.

The number of acid sites of these Mⁿ⁺-monts was tentatively estimated for convenience by the previously described NH₃-TPD method.⁶ Although the number of acid sites in the Mⁿ⁺-mont determined by NH₃-TPD may not accurately represent the active acid sites available to this reaction, it provides a reference for the number of acid sites in Mⁿ⁺-mont. For example, the number of acid sites on Zr⁴⁺-mont was 0.734 mmol g⁻¹.⁶ We also estimated the amount of active acid sites of Zr⁴⁺-mont by poisoning it with triethylamine in the carbonyl-ene reaction system according to a previously reported method.^{7,8} The number of acid sites of Zr⁴⁺-mont was 0.749 mmol g⁻¹ (Fig. 1), which was quite similar to that obtained by NH₃-TPD analysis. Additionally, the amount of Zr⁴⁺ cations of Zr⁴⁺-mont was estimated by X-ray fluorescence (XRF) analysis⁹ to be 1.683 mmol g⁻¹, indicating that sufficient Zr⁴⁺ cations are present to work as Lewis acid sites.

Intramolecular carbonyl-ene reaction of citronellals in the presence of Mⁿ⁺-mont

Since K-10 mont has been known to catalyse the cyclization of citronellal,⁵ we applied this Zr⁴⁺-mont catalytic system to

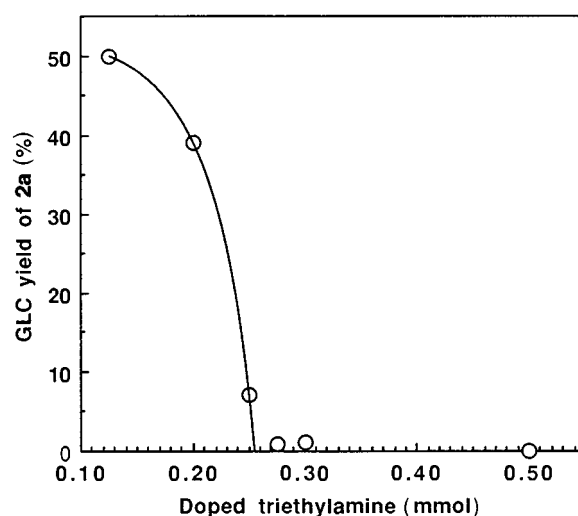


Fig. 1 The GLC yield of 3-phenylbut-3-en-1-ol **2a** in the carbonyl-ene reaction of α -methylstyrene **1a** (5 mmol) with paraformaldehyde (10 mmol) in acetonitrile (10 cm³) in the presence of Zr⁴⁺-mont (340.6 mg) and various amounts of triethylamine at 80 °C for 24 h (○)

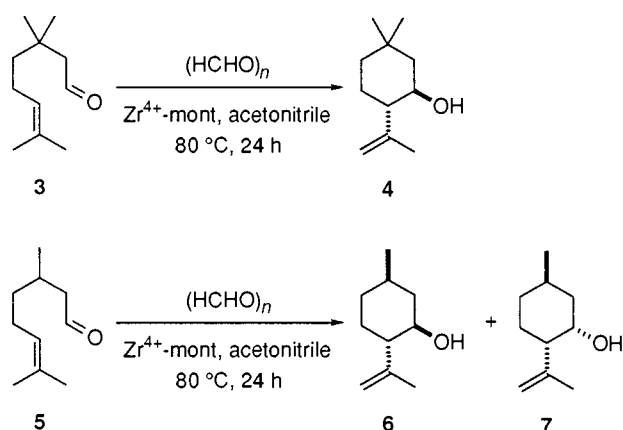
citronellals hoping for an intramolecular cyclization (Scheme 2). Typical results are shown in Table 2 together with the results of the corresponding control experiments. The expected intramolecular carbonyl-ene reaction occurred with 3,3,7-trimethyloct-6-enal (3-methylcitronellal) **3** and 3,7-dimethyloct-6-enal (citronellal) **5** to provide the corresponding cyclized compounds highly stereoselectively and in high yield. Thus, from **3**, only 2-isopropenyl-5,5-dimethylcyclohexanol (methylisopulegol) **4** was formed in 94% yield (run 1), while, from **5**, a mixture of 2-isopropenyl-5-methylcyclohexanols [**6** (isopulegol) and **7** (neo-isopulegol)] was obtained in 91% yield (**6**:**7** = 90:10) ‡ (run 7). The turnover numbers were calculated as 19 and 18 based on the amount of acid sites of Zr⁴⁺-mont estimated by NH₃-TPD analysis,⁶ respectively. The catalyst could

‡ With Fe³⁺-mont, 82% yield (94:6); with Al³⁺-mont, 60% yield (92:8); with Ce³⁺-mont, 80% yield (96:4).

Table 2 Metal cation-exchanged montmorillonite (M^{n+} -mont)-catalysed carbonyl-ene reaction of citronellals*

Run	Citronellals	M^{n+} -mont	(w/mg)	Product	Yield (%) ^a
1	3	Zr ⁴⁺	(340.6)	4	94
2 ^b	3	Zr ⁴⁺	(340.6)	4	54
3 ^c	3	Zr ⁴⁺	(340.6)	4	99
4	3	H ⁺ (K10)	(788.6)	4	55
5	3	Na ⁺	(500.0)	—	0
6	3	—	—	—	0
7	5	Zr ⁴⁺	(340.6)	6 + 7	91 (90:10)
8	5	Zr ⁴⁺ (2nd)	(340.6)	6 + 7	98 ^d
9	5	Zr ⁴⁺ (3rd)	(340.6)	6 + 7	92 ^d
10	5	Zr ⁴⁺ (4th)	(340.6)	6 + 7	93 ^d
11	5	Zr ⁴⁺ (5th)	(340.6)	6 + 7	89 ^d
12 ^e	5	Zr ⁴⁺	(3406.0)	6 + 7	85 (92:8)
13	5	H ⁺ (K10)	(788.6)	6 + 7	41 (90:10)
14	5	Na ⁺	(500.0)	—	0
15	5	—	—	—	0
16 ^b	5	Zr ⁴⁺	(340.6)	6 + 7	31 (90:10)
17 ^f	5	Zr ⁴⁺	(340.6)	6 + 7	98 (90:10)

* *Reagents and conditions:* Citronellals (5 mmol) and M^{n+} -mont (0.25 mmol as acid sites estimated by NH_3 -TPD analysis) in acetonitrile (10 cm³) at 80 °C for 24 h. ^a Yield of an isolated pure compound, based on **1**, except otherwise noted. The ratio of **6**:**7** estimated by ¹H NMR spectroscopy is shown in parenthesis. ^b At 25 °C for 24 h. ^c At 80 °C for 1.5 h. ^d GLC yield. ^e The reaction on a 10-fold scale. ^f At 80 °C for 3 h.

**Scheme 2**

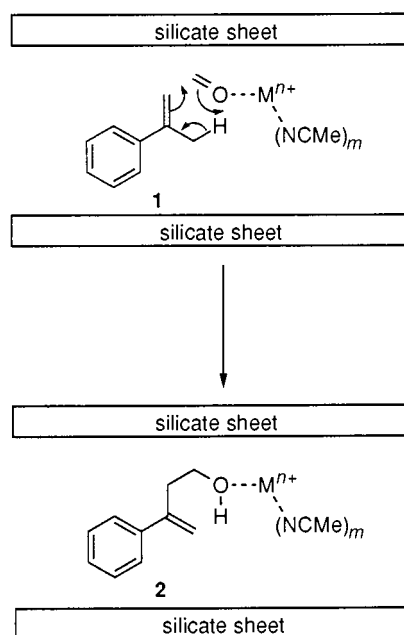
be re-used at least 5 times almost without loss of activity by treatment of the recovered catalyst as described in a former section (runs 7–11). For practical purposes, the carbonyl-ene reaction of compound **5** was carried out on a scale 10-fold that of a typical procedure; a mixture of **6** and **7** (isomer ratio, 92:8) was isolated by distillation in 85% yield (run 12). This intramolecular cyclization was quite fast compared with the intermolecular reaction and the reaction time of 1.5–3 h at 80 °C was enough to complete the reaction (runs 3 and 17). The reaction proceeded even at 25 °C, although it was slightly slower (run 2). H⁺-Mont was only slightly effective (runs 4 and 13), although no reaction occurred when Na⁺-mont was used or there was no catalyst (runs 5, 6, 14 and 15). The cyclization did not occur at all with alkenyl esters such as 6-acetoxyhex-1-ene and 2,6-dimethyl-8-acetoxyoct-2-ene (citronellal acetate) in the presence of Zr⁴⁺-mont even at 80 °C for 24 h, all the esters being recovered unchanged.

The high stereoselectivity observed here in the cyclization of citronellal **5** is worth noting, since many reported procedures using a variety of reagents and catalysts such as Zn/Me₃SiCl,¹⁰ zeolites,¹¹ SmI₂,¹² Cu-Cr¹³ and Me₂AlCl¹⁴ and also thermal cyclization^{10,15} resulted in either formation of mixtures of low selectivity or sometimes in lower yields; exceptions to this were when zinc halide,¹⁶ SiO₂/Al₂O₃¹⁷ and Zr(SO₄)₂¹⁷ were used where the ratio of **6** to other diastereoisomers was reported to be 88–96/4–12.

Plausible reaction pathway

M^{n+} -monts have been shown 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 clay skeleton.¹⁸ A proposed reaction pathway between α -methylstyrene **1a** and paraformaldehyde in the interlayer space is shown in Scheme 3 where **1a** reacted

**Scheme 3**

concertedly with monomeric formaldehyde. Here, the exchanged metal cations in the interlayer space were coordinated by acetonitrile molecules instead of water molecules and the cations worked as Lewis acids in contrast to the Prins reaction where water molecule on cations of M^{n+} -mont worked as a Brønsted acid.³ Monomeric formaldehyde might be produced in solution by the decomposition of paraformaldehyde due to an interaction with the acid sites of the clay surface.

Restriction of the reaction field in the interlayer space between two aluminosilicate sheets as well as a Lewis acid-catalysed concerted cyclization (not a Brønsted acid-catalysed stepwise reaction) might give a high stereoselectivity in the cyclization of **3** and **5**, though the details are not yet known.

Conclusion

Metal cation-exchanged montmorillonite (M^{n+} -mont) worked as a Lewis acid in acetonitrile to induce the intermolecular

carbonyl-ene reaction of α -methylstyrenes with paraformaldehyde as well as the intramolecular reaction of citronellals, Zr⁴⁺-mont being the catalyst of choice. A Brønsted acidic Mⁿ⁺-mont was converted into a Lewis acidic Mⁿ⁺-mont when the solvent was changed from toluene or 1,4-dioxane to acetonitrile. Although the number of alkenes and aldehydes to which this reaction is applicable is limited, the high stereoselectivity achieved in the cyclization of citronellals as well as the re-use of the catalyst without a loss of activity indicate that this catalytic reaction has merit.

Experimental

NMR spectra were recorded on JEOL EX-400 (¹H, 400 MHz; ¹³C, 100 MHz) and JEOL GSX-270 (¹H, 270 MHz; ¹³C, 67.8 MHz) spectrometers for solutions in CDCl₃ with Me₄Si 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 and br = broad. Mass spectra were measured on Shimadzu QP-5000S mass spectrometer equipped with a Shimadzu GC-17 gas-liquid chromatograph (30 m × 0.254 mm, 0.25 μm film thickness, J&W Scientific fused silica capillary column DB-1). The electron-impact (EI) method was used for ionization and the ionizing voltage was 70 eV for all compounds. GLC analyses were performed on a Shimadzu GC-14A instrument (25 m × 0.33 mm, 5.0 μm film thickness, a Shimadzu fused silica capillary column HiCap CBP10-S25-050) with flame-ionization detectors and helium as carrier gas. Recycling preparative high performance liquid chromatography (HPLC) was performed on a JAI LC-908-G30 instrument (600 × 20 mm × 2, JAIGEL-1H and JAIGEL-2H dual styrene polymer columns) equipped with an ultraviolet (UV) and refractive-index (RI) detector and CHCl₃ as eluent. Column chromatography on SiO₂ was performed with Wakogel[®] C-300 (hexane, hexane-ethyl acetate and ethyl acetate as eluents). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

All commercially available organic and inorganic compounds were used without further purification except for the solvent, which was dried and distilled by the known method before use.¹⁹ Montmorillonite K10, namely H⁺-mont, was commercially available from Aldrich Chemical Co., Inc., which was used as obtained. Kunipia[®] G, namely Na⁺-mont, was obtained from Kunimine Industries Co., Ltd. Mⁿ⁺-Mont (Mⁿ⁺ = Zr⁴⁺, Al³⁺, Fe³⁺, Ce³⁺, Zn²⁺) was prepared by stirring Na⁺-mont with the corresponding metal oxychloride or nitrate in aqueous acetone at 50 °C for 24 h after which the product was collected, washed with pure water and dried as described previously.^{8,20}

Compounds **1a**, **1e** and **5** are commercially available. Compounds **1b**,^{21,22} **1c**,^{21,22} **1d**^{21,22} and **1f**²²⁻²⁴ were synthesized by a literature method with slight modification. Compound **3** was prepared by a literature method.²⁵ Compounds **2a**,^{26,27} **2c**,²⁸ **2d**,²⁸ **2e**,²⁹ **4**²⁵ and **6**¹⁵ are known compounds and identified from their spectral data. New spectral data for the compounds are shown below. Compounds **2b** and **2f** which are new compounds were characterized from their spectral data.

p-Methoxy- α -methylstyrene **1b**^{21,22}

To a mixture of *p*-methoxyacetophenone (4.93 g, 30.0 mmol) and dry THF (100 cm³) was added dropwise a THF solution of methylmagnesium bromide [1.32 M (1 M = 1 mol dm⁻³); 53 mmol, 40 cm³] during 1 h at room temperature with magnetic stirring. The mixture was refluxed for 24 h with stirring and then poured into ice-water (100 cm³). The mixture was then treated with 20% aqueous H₂SO₄ (200 cm³). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 100 cm³). The combined organic layer and extracts were washed with brine (100 cm³), dried (MgSO₄) and concentrated. The resulting colourless oil, 2-(*p*-methoxyphenyl)propan-2-ol in quantitative yield, was diluted with 20%

aqueous H₂SO₄ (200 cm³) and the mixture was refluxed for 2 h. After it had been cooled, the mixture was extracted with diethyl ether (3 × 100 cm³). The combined ethereal extracts were washed with brine (100 cm³), dried (MgSO₄) and evaporated to afford a pale yellow oil, which was bulb-to-bulb distilled to give the desired *p*-methoxy- α -methylstyrene **1b** as a colourless oil (1.48 g, 10.0 mmol, 33% isolated yield).

p-Methyl- α -methylstyrene **1c**^{21,22}

This compound was similarly prepared from *p*-methylacetophenone in 59% isolated yield.

p-Bromo- α -methylstyrene **1d**^{21,22}

This compound was similarly prepared from *p*-bromoacetophenone in 51% isolated yield.

p-Trifluoromethyl- α -methylstyrene **1f**²²⁻²⁴

To a mixture of *p*-trifluoromethylbenzoic acid (11.41 g, 60.0 mmol), ethanol (5.53 g, 120.0 mmol) and dry dichloromethane (100 cm³) was added dropwise concentrated H₂SO₄ (3 cm³) at room temperature with stirring. The mixture was refluxed for 15 h. After it had been cooled, the mixture was washed with saturated NaHCO₃ (3 × 100 cm³) and brine (100 cm³), dried (MgSO₄) and evaporated to afford a colourless liquid. This was subjected to column chromatography [Wakogel[®] C-300; eluents, hexane, hexane-ethyl acetate (9:1) and ethyl acetate] to provide ethyl *p*-trifluoromethylbenzoate as a colourless oil (9.04 g, 34.2 mmol, 57% isolated yield).

To a stirred and refluxing mixture of methyl iodide (7.28 g, 51.3 mmol), magnesium (1.25 g, 51.3 mmol) and dry diethyl ether (100 cm³) was added dropwise ethyl *p*-trifluoromethylbenzoate (9.04 g, 34.2 mmol) in dry diethyl ether (100 cm³). The mixture was stirred magnetically at the reflux temperature for 24 h, after which it was cooled, treated with aqueous ammonium chloride (200 cm³) and extracted with diethyl ether (3 × 100 cm³). The combined ethereal extracts were washed with brine (100 cm³), dried (MgSO₄) and evaporated to leave a colourless oil. This was subjected to column chromatography [Wakogel[®] C-300; eluents, hexane, hexane-ethyl acetate (9:1) and ethyl acetate] to provide a colourless oil of 2-(4-trifluoromethylphenyl)propan-2-ol (6.38 g, 33.2 mmol, 97% isolated yield).

A magnetically stirred mixture of the resulting oil (6.38 g, 33.2 mmol) and 20% aqueous H₂SO₄ (200 cm³) was refluxed for 2 h after which it was cooled and extracted with diethyl ether (3 × 100 cm³). The ethereal extract was washed with brine (100 cm³), dried (MgSO₄) and concentrated to afford a residue which upon distillation under reduced pressure provided a colourless oil. The desired *p*-trifluoromethyl- α -methylstyrene **1f** was isolated in a pure form by successive recycling preparative HPLC (1.36 g, 7.3 mmol, 22% isolated yield).

General procedure for metal cation-exchanged montmorillonite-(Mⁿ⁺-mont)-catalysed intermolecular carbonyl-ene reaction of α -methylstyrenes with paraformaldehyde

A typical experimental procedure was as follows (Table 1, run 1). To a mixture of α -methylstyrene **1a** (590.9 mg, 5.0 mmol), dry acetonitrile (10 cm³) and paraformaldehyde (300.4 mg, 10.0 mmol) was added Zr⁴⁺-mont (340.6 mg, 0.25 mmol as acid sites estimated by NH₃-TPD analysis) at 25 °C with magnetic stirring. The resulting mixture was stirred at 80 °C for 24 h, after which it was cooled and suction-filtered to recover the catalyst (Toyo, quantitative filter paper No. 4A); the recovered catalyst was then rinsed with diethyl ether (10 cm³). The combined filtrate and ethereal washings were evaporated under reduced pressure to leave a colourless oil. This was subjected to silica-gel column chromatography (Wakogel[®] C-300; eluents, hexane and then hexane-ethyl acetate = 95:5) to give unchanged **1a** [141.8 mg, 1.20 mmol by GLC (hexane)] and 3-phenylbut-3-en-1-ol **2a** [452 mg, 3.05 mmol, 61% yield

(hexane–ethyl acetate)] which contained small amounts of the formate of **2a** as well as uncharacterized compounds. Further purification (hexane–ethyl acetate) afforded pure 3-phenylbut-3-en-1-ol **2a** as a colourless oil (348.3 mg, 2.35 mmol, 47% isolated yield), which was identified upon the basis of spectral results: δ_{H} (270 MHz) 2.06 (1H, s, br, OH), 2.75 (2H, td, J 6.4, 0.99, CH_2), 3.68 (2H, t, J 6.4, CH_2OH), 5.12 (1H, dt, J 1.49, 0.99, $\text{C}=\text{CH}_2$), 5.38 (1H, d, J 1.49, $\text{C}=\text{CH}_2$) and 7.20–7.41 (5H, m, ArH); δ_{C} (67.8 MHz) 38.5 (t), 60.9 (t), 114.4 (t), 126.1 (d), 127.6 (d), 128.4 (d), 140.5 (s) and 144.8 (s); m/z 148 (M^+ , 26%), 133 (20), 117 (35), 103 (29), 91 (30), 78 (100) and 51 (40).

The recovered Zr^{4+} -mont was regenerated by stirring it magnetically with 50% aqueous acetone (10 cm^3) at room temperature for 24 h after which it was filtered and dried at 120 °C in an electric oven for 24 h.

3-(4-Methoxyphenyl)but-3-en-1-ol 2b. A white solid: mp 42.5–44.0 °C; δ_{H} (270 MHz) 1.82 (1H, s, br, OH), 2.76 (2H, td, J 6.4, 1.1, CH_2), 3.72 (2H, t, J 6.4, CH_2OH), 3.81 (3H, s, CH_3O), 5.07 (1H, dt, J 1.4, 1.1, $\text{C}=\text{CH}_2$), 5.34 (1H, d, J 1.4, $\text{C}=\text{CH}_2$), 6.86 (2H, d, J 8.79, ArH, AA'XX' type) and 7.35 (2H, d, J 8.79, ArH, AA'XX' type); δ_{C} (67.8 MHz) 38.6 (t), 55.3 (q), 61.0 (t), 76.5 (t), 77.5 (d), 127.2 (d), 132.7 (s), 144.0 (s) and 159.3 (s); m/z 178 (M^+ , 61%), 163 (19), 148 (17), 135 (100), 115 (26), 108 (44), 91 (30), 77 (35), 55 (29) and 51 (25) (Found: C, 73.5; H, 8.0. $\text{C}_{11}\text{H}_{14}\text{O}_2$ requires C, 74.12; H, 7.92%).

3-(4-Methylphenyl)but-3-en-1-ol 2c. A colourless oil; δ_{H} (270 MHz) 2.16 (1H, s, br, OH), 2.34 (3H, s, CH_3), 2.77 (2H, td, J 6.3, 1.1, CH_2), 3.72 (2H, t, J 6.3, CH_2OH), 5.11 (1H, d, J 1.4, $\text{C}=\text{CH}_2$), 5.38 (1H, d, J 1.4, $\text{C}=\text{CH}_2$), 7.13 (2H, d, J 8.24, ArH, AA'BB' type) and 7.31 (2H, d, J 8.24, ArH, AA'BB' type); δ_{C} (67.8 MHz) 20.7 (q), 38.1 (t), 60.7 (t), 113.0 (t), 125.6 (d), 128.8 (d), 136.9 (s), 137.3 (s) and 143.3 (s); m/z 162 (M^+ , 61%), 147 (57), 129 (38), 115 (68), 105 (27), 92 (100), 77 (22), 65 (32) and 51 (28).

3-(4-Bromophenyl)but-3-en-1-ol 2d. A colourless oil; δ_{H} (270 MHz) 2.17 (1H, s, br, OH), 2.75 (2H, td, J 6.2, 1.0, CH_2), 3.72 (2H, t, J 6.2, CH_2OH), 5.18 (1H, d, J 1.1, $\text{C}=\text{CH}_2$), 5.40 (1H, d, J 1.1, $\text{C}=\text{CH}_2$), 7.28 (2H, d, J 8.5, ArH, AA'BB' type) and 7.46 (2H, d, J 8.5, ArH, AA'BB' type); δ_{C} (67.8 MHz) 38.2 (t), 60.8 (t), 114.9 (t), 121.5 (s), 127.7 (d), 131.4 (d), 139.3 (s) and 143.7 (s); m/z 226 (M^+ , 26%), 211 (17), 196 (12), 183 (26), 169 (5), 156 (16), 147 (23), 129 (30), 115 (100), 102 (31), 91 (21), 77 (21), 63 (21) and 51 (34).

3-(4-Chlorophenyl)but-3-en-1-ol 2e. A colourless oil; δ_{H} (400 MHz) 2.12 (1H, s, br, OH), 2.72 (2H, t, J 6.8, CH_2), 3.68 (2H, t, J 6.4, CH_2OH), 5.14 (1H, d, J 0.9, $\text{C}=\text{CH}_2$), 5.38 (1H, d, J 0.9, $\text{C}=\text{CH}_2$) and 7.27–7.33 (4H, m, ArH); δ_{C} (67.8 MHz) 38.3 (t), 60.8 (t), 114.9 (t), 127.4 (d), 128.5 (d), 133.4 (s), 138.9 (s) and 143.7 (s); m/z 182 (M^+ , 46%), 167 (41), 151 (39), 139 (44), 129 (39), 112 (100), 101 (28), 75 (45), 62 (35) and 51 (54).

3-(4-Trifluoromethylphenyl)but-3-en-1-ol 2f. A colourless oil; δ_{H} (270 MHz) 2.06 (1H, s, br, OH), 2.77 (2H, td, J 6.3, 1.0, CH_2), 3.74 (2H, t, J 6.3, CH_2OH), 5.27 (1H, d, J 1.3, $\text{C}=\text{CH}_2$), 5.47 (1H, d, J 1.3, $\text{C}=\text{CH}_2$), 7.51 (2H, d, J 8.24, ArH, AA'BB' type) and 7.59 (2H, d, J 8.24, ArH, AA'BB' type); m/z 216 (M^+ , 45%), 201 (58), 185 (56), 166 (35), 165 (49), 146 (56), 133 (19), 115 (91), 109 (14), 89 (10), 75 (22), 63 (18) and 51 (40).

General procedure for metal cation-exchanged montmorillonite (M^{n+} -mont)-catalysed intramolecular carbonyl-ene reaction of citronellals

A typical experimental procedure was as follows (Table 2, run 3). To a mixture of 3-methylcitronellal **3** (841.4 mg, 5.0 mmol) and dry acetonitrile (10 cm^3) was added Zr^{4+} -mont (340.6 mg, 0.25 mmol as acid sites estimated by NH_3 -TPD analysis) at 25 °C. The resulting mixture was stirred magnetically at 80 °C for 1.5 h after which it was cooled and suction-filtered to recover the catalyst (Toyo, quantitative filter paper No. 4A); the

catalyst was then rinsed with diethyl ether (10 cm^3). Evaporation of combined filtrate and the ethereal washings under reduced pressure left a colourless oil, which was subjected to silica-gel column chromatography (Wakogel® C-300; eluents, hexane, hexane–ethyl acetate = 95:5 and then ethyl acetate). Concentration of the fractions of hexane–ethyl acetate afforded a colourless oil of methylisopulegol **4** (833.0 mg, 4.95 mmol, 99%) which was identified upon the basis of spectral results.²⁵

Compounds **6** and **7** obtained from citronellal **5** were similarly isolated by silica-gel column chromatography (Wakogel® C-300; hexane–ethyl acetate = 95:5 as eluent) as a mixture: the ratio of the two compounds was measured by ^1H NMR spectroscopy:¹⁵ compound **6**: δ_{H} 0.938 (d, J 6.75, CH_2CH), 3.455 (td, J 10.0 and 4.0, CHOH); compound **7**: δ_{H} 0.880 (d, J 6.75, CH_2CH) and 3.710 (td, J 10.0 and 4.0, CHOH). Since chemical shift and coupling constant values are slightly different from those reported in the literature,¹⁵ we cannot exclude the possibility that the minor compound **7** tentatively assigned here might be iso-isopulegol where both isopropenyl and methyl groups are in a *trans* disposition to a hydroxy group. The products of a 10-fold scale reaction using **5** (7.70 g, 50 mmol) and Zr^{4+} -mont (3.406 g) in acetonitrile (100 cm^3) were isolated by distillation as a colourless oil (6.545 g, 42.5 mmol, 85% yield): bp 75–76 °C (7 mmHg); lit.,³⁰ 88 °C (10 mmHg).

Estimation of the number of active acid sites on Zr^{4+} -mont with triethylamine-doped acetonitrile (Fig. 1)

Following a literature method,^{7,8} we stirred magnetically a mixture of freshly prepared triethylamine-doped acetonitrile (10.0 cm^3 ; containing various amounts of triethylamine) and Zr^{4+} -mont (340.6 mg) at room temperature for 3 h. To the mixture were added paraformaldehyde (300.4 mg, 10.0 mmol) and α -methylstyrene **1a** (590.9 mg, 5.0 mmol). The mixture was stirred first at room temperature for 5 min and then at 80 °C for 24 h. After it had been cooled, the reaction mixture was suction-filtered to remove the catalyst which was then rinsed with diethyl ether (10 cm^3). Acetophenone was added to a mixture of the filtrate and the washings as an internal standard and the amount of **2a** produced was estimated by GLC analysis.

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