Direct chlorination of alcohols with chlorodimethylsilane catalyzed by a gallium trichloride/tartrate system under neutral conditions†

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Received 17th March 2008, Accepted 18th April 2008
First published as an Advance Article on the web 28th May 2008
DOI: 10.1039/b804589e

The reaction of secondary alcohols **1** with chlorodimethylsilane ($HSiMe_2Cl$) proceeded in the presence of a catalytic amount of $GaCl_3$/diethyl tartrate to give the corresponding organic chlorides **3**. In the catalytic cycle, the reaction of diethyl tartrate **4a** with $HSiMe_2Cl$ **2** gives the chlorosilyl ether **5** with generation of H_2. Alcohol-exchange between the formed chlorosilyl ether **5** and the substrate alcohol **1** affords alkoxychlorosilane **6**, which reacts with catalytic $GaCl_3$ to give the chlorinated product **3**. The moderate Lewis acidity of $GaCl_3$ facilitates chlorination. Strong Lewis acids did not give product due to excessive affinity for the oxy-functionalities. Although tertiary alcohols were chlorinated by this system even in the absence of diethyl tartrate, certain alcohols that are less likely to give carbocationic species were effectively chlorinated using the $GaCl_3$/diethyl tartrate system.

Introduction

Chlorination of alcohols is an important process in organic transformation. There are numerous chlorination systems, but most of them are employed under acidic conditions.[1] Therefore, substrate selection is severely limited and development of chlorination systems that operate under neutral conditions is required. Recently, we reported a neutral system for chlorination of alcohols using dimethylchlorosilane ($HSiMe_2Cl$) and an $InCl_3$ catalyst.[2] However, this system requires an equimolar amount of benzil to avoid background reduction of the alcohol.[3] To the best of our knowledge, a completely catalytic system for direct chlorination of a wide range of alcohol substrates under neutral conditions has never been realized.

Chlorohydrosilane ($HSiR_2Cl$) has interesting structural features. In particular, the silicon center has two reactive sites – hydrogen and chlorine – either of which can be utilized for organic transformations. Both chlorosilane (R_3SiCl) and hydrosilane (R_3SiH) react with alcohols to give silyl ethers in the presence of either promoters or catalysts.[4,5] Both chlorohydrosilane ($HSiR_2Cl$) sites react with diols to give cyclic silanes.[6] The selective reaction of $HSiR_2Cl$ at only the Si–H site prior to reaction with the Si–Cl site is a difficult problem. The reaction of chlorohydrosilanes ($HSiR_2Cl$) with alcohols is effectively catalyzed by $InCl_3$to give a reduced product (alkane) **D** through hydrosilyl ether **A** with release of HCl. In this reaction, Si–Cl reacts prior to reaction with Si–H.[3] During chlorination, formation of chlorosilyl ether **B** necessitates H_2 release, although this phenomenon is rarely observed. Thus, we were motivated to develop a new, effective catalytic system that yields **B**. A dummy alcohol (R′OH) that favors production of H_2 over HCl when reacted with chlorohydrosilane would give a route to chlorosilyl ether **C**, followed by alcohol-exchange to give the chloride **E** *via* **B**. Moreover, R′OH should not give the chloride, R′Cl, under these conditions. In this paper, we report $GaCl_3$-catalyzed direct chlorination of alcohols with chlorohydrosilane using tartrate as a dummy alcohol.

Results and discussion

Optimization of catalytic chlorination of alcohol

Table 1 summarizes optimization of the catalyst system for the reaction of 4-phenyl-2-butanol **1a** with chlorodimethylsilane ($HSiMe_2Cl$) **2**. After testing many alcohols, diethyl tartrate was found to be effective in the synthesis of the chlorinated product. As shown in entry 2, combined use of 10 mol% of diethyl tartrate **4a** and 5 mol% of $GaCl_3$ effectively catalyzed the reaction to give the corresponding chloride **3a**.[7] As the reaction progressed, generation of H_2 gas was observed. Exclusive use of $GaCl_3$ or tartrate **4a** did not yield the product (entries 1 and 8). $GaBr_3$, GaI_3, or $Ga(OTf)_3$ showed low product yields (entries 4–6). $InCl_3$ also acted as a catalyst, giving **3a**, but in lower yield (entry 7). The amount of **4a**, an R′OH, was important as loading of 50 mol% of **4a** gave a low yield (entry 3). Other metal halides, such as $AlCl_3$, $ZnCl_2$, $TiCl_4$, or $BiCl_3$, were examined, but did not yield the product (entries 9–12). An α-hydroxyl carbonyl unit in the alcohol (R′OH) is indispensable. Both hydroxyl ester **4b** and ketone **4c** gave the product when the $GaCl_3$ catalyst was used, although the yields were low (entries 13 and 14). Neither benzoin ethyl ether **4d** (containing a protected hydroxy carbonyl group) nor the diol **4e** showed catalytic activity.

Chlorination of secondary alcohols catalyzed by the $GaCl_3$/tartrate system

Next, we explored the generality of the $GaCl_3$/tartrate-catalyzed reaction with chlorodimethylsilane by testing different alcohols

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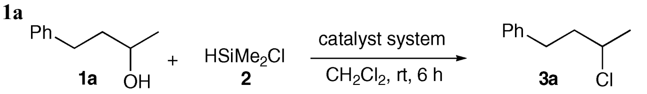
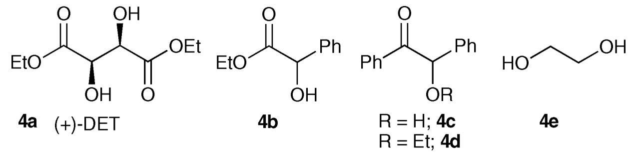
† Electronic supplementary information (ESI) available: Experimental procedures. See DOI: 10.1039/b804589e

Table 1 Optimization of the catalyst system for chlorination of alcohol **1a**

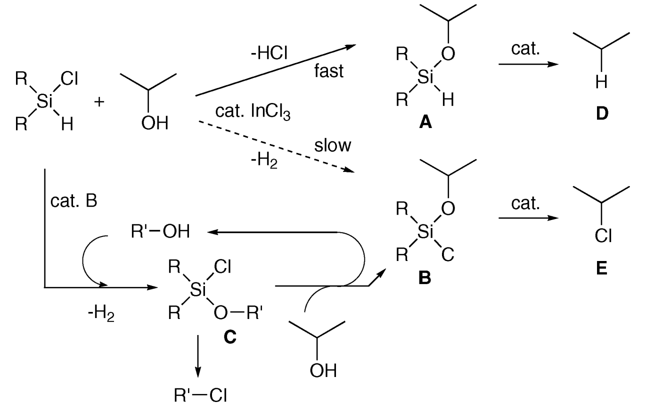


Entry	Catalyst system R′OH (10 mol%)	Metal halide (5 mol%)	Yield (%)
1	None	$GaCl_3$	0
2	**4a**	$GaCl_3$	75
3	**4a** (50 mol%)	$GaCl_3$	19
4	**4a**	$GaBr_3$	35
5	**4a**	GaI_3	15
6	**4a**	$Ga(OTf)_3$	4
7	**4a**	$InCl_3$	28
8	**4a**	None	0
9	**4a**	$AlCl_3$	0
10	**4a**	$ZnCl_2$	0
11	**4a**	$TiCl_4$	0
12	**4a**	$BiCl_3$	0
13	**4b**	$GaCl_3$	19
14	**4c**	$GaCl_3$	65
15	**4d**	$GaCl_3$	0
16	**4e**	$GaCl_3$	0

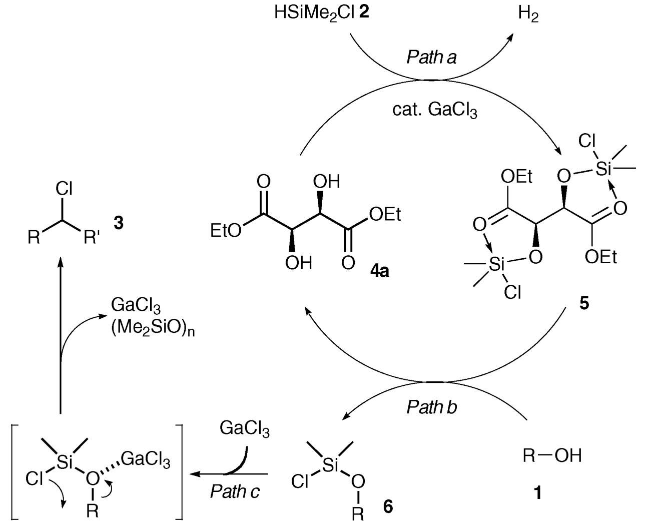


(Table 2). Various secondary alcohols were effectively converted to the corresponding chlorides, while primary alcohols did not yield the product.[8] The reaction of 2-octanol **1b** afforded the 2-chlorooctane **3b** in moderate yield with some unidentified rearranged chlorides (entry 2). The elemental analysis of the mixture of the products showed good agreement with chlorooctane. The ratio of **3b** to byproducts is almost 1 : 0.6 by NMR. This result suggests that our system includes cationic mechanism that often gives rearranged isomers. Cyclohexanol **1c** exclusively gave the chlorocyclohexane **3c** (entry 3). 2-Adamantanol **1d**, 3-phenyl-2-propanol **1e** and 2-butanol **1f** gave the corresponding chlorides in high yields (entries 4–6). The acid-sensitive substrate **1g** exclusively gave the corresponding product **3g** without any contamination because the system was employed under neutral conditions (entry 7). Substrate **1h**, bearing both secondary and primary hydroxyl sites, was chlorinated exclusively at the secondary site (entry 8). In contrast, conventional chlorination of **1h** using a Ph_3P/CCl_4 system afforded 13-chloro-2-tridecanol (81% yield) *via* reaction at a primary OH group. Our system was selective for chlorination of polyols. The *N*-phthaloyl-substituted starting alcohol **1i** was effectively transformed into the chloride form, while the nitrogen moiety was not involved in the reaction (entry 9).

Investigation of reaction mechanism



Scheme 1 Catalytic chlorination mediated by a dummy alcohol (R′OH).

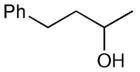
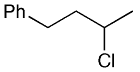
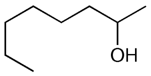
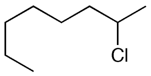
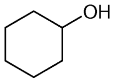
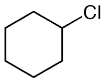
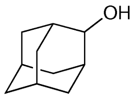
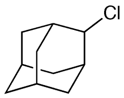
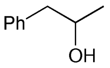
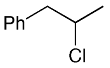
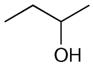
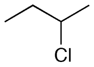
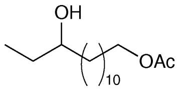
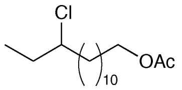
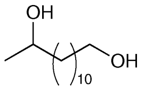
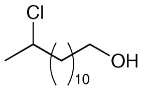
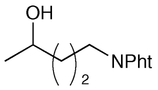
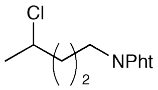


Scheme 2 Plausible reaction mechanism.

A plausible reaction mechanism is shown in Scheme 2. Diethyl tartrate **4a** acts as a dummy alcohol (R′OH), as shown in Scheme 1, and gives chlorosilyl ether **5** and H_2 as a byproduct (path a). Compound **5** undergoes alcohol-exchange with the substrate alcohol **1** to form chlorosilyl alkoxide **6** with regeneration of **4a** (path b). The chlorosilyl alkoxide **6** is catalyzed by $GaCl_3$ to give the chlorinated product **3** with siloxane release (path c). Among paths a–c, path a is crucial. We sought dummy alcohols (R′OH) that favor production of H_2 over HCl during generation of chlorosilyl ethers. In addition, the formed chlorosilyl ether should not transform into chloride. The tartrate **4a** satisfies these requirements for the dummy alcohol. Typically, formation of hydrosilyl ether with generation of HCl is kinetically favored; this was the only reaction observed during the reaction of benzhydrol with chlorohydrosilane.[3] In the case of tartrate, however, chlorosilyl ether **5** forms with evolution of H_2. Even if the hydrosilyl ether was generated, transformation into the reduced tartrate would not take place because the carbocation generated with assistance from $GaCl_3$ is destabilized by the electron-withdrawing carbonyl group in **4a**. The pathway to the hydorosilyl ether is reversible; therefore, the irreversible and thermodynamically favorable pathway to the chlorosilyl ether proceeds, giving H_2. The chlorosilyl ether **5** does not form chlorinated tartrate, also due to destabilization of the carbocation. Thus, **4a** appears to be a suitable dummy alcohol, although direct evidence is yet to be obtained.

We confirmed each step for paths a–c of the catalytic cycle shown in Scheme 2. *Path a*: A 1 : 2 mixture of **4a** and **2** in the presence of 5 mol% of $GaCl_3$ generated H_2 gas and gave the starting material **4a**, after aqueous work-up. The corresponding

Table 2 Chlorination of secondary alcohols **1**[a]

Entry	Alcohol	Time/h	Product	Yield (%)
1	 **1a**	6	 **3a**	75
2	 **1b**	4	 **3b**	36
3	 **1c**	14	 **3c**	57
4	 **1d**	24	 **3d**	89
5	 **1e**	1	 **3e**	69
6	 **1f**	4	 **3f**	62[b]
7	 **1g**	20	 **3g**	53
8[c]	 **1h**	24	 **3h**	39
9	 **1i**	24	 **3i**	84

[a] All reactions were carried out at room temperature in CH_2Cl_2 with 1.0 equiv of alcohol **1**, 1.3 equiv of $HSiMe_2Cl$ **2**, 5 mol% of $GaCl_3$, and 10 mol% of diethyl tartrate **4a**. [b] Direct observation of the product by NMR because of the high volatility of **3f**. [c] $HSiMe_2Cl$ (3.0 equiv) was used.

reduced or chlorinated compounds did not form, probably because the carbocation at the α-position of the carbonyl is unstable. This result suggests generation of chlorosilyl ether **5**. In fact, NMR analysis of the reaction mixture prior to work-up indicated generation of **5** (eqn 1, Fig. 1-ii). The OCH_2Me signal appeared as an ABq when irradiated at the Me group, presumably because of a rigid structure caused by Si-chelation in **5**. ^{29}Si NMR showed a reasonable chemical shift at 7.53 ppm without $^1J_{SiH}$ coupling. Since the use of Et_3SiH instead of $HSiMe_2Cl$ resulted in slow generation of H_2 under the same conditions, chlorine on Si must be important for the formation of the silyl ether. $GaCl_3$ is indispensable in this step because a control experiment, in which the $GaCl_3$-catalyst was not used, did not give **5**. *Path b*: Addition of 1-octanol to the generated species **5** afforded a mixture of $Me_2(OctO)SiCl$ **7** and **4a** by alcohol-exchange (eqn 2).[10] The species formed showed ^1H, ^{13}C, and ^{29}Si NMR signals comparable to those reported for similar compounds (Fig. 1(iii)).[11] *Path c*: The isolated chlorosilyl ether **9** reacted with catalytic $GaCl_3$ (5 mol%) to give the chloride **3a** in 62% yield (eqn 3). These results provide strong support for the reaction course illustrated in Scheme 2.

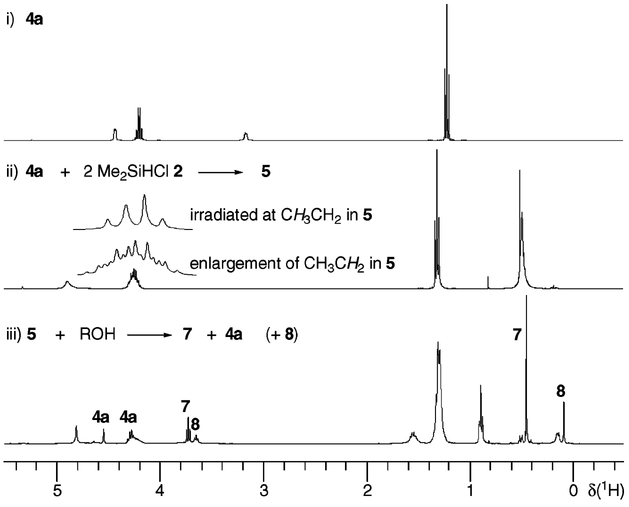
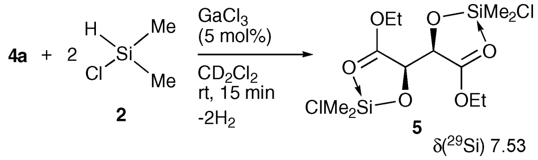
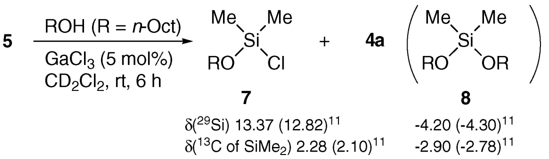


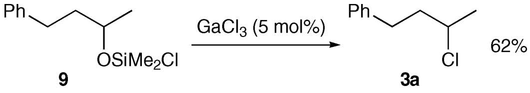
Fig. 1 NMR study for mechanistic investigation (CD_2Cl_2). *Reagents and conditions*: (i) diethyl tartrate **4a**. (ii) 2 : 1 mixture of $HSiMe_2Cl$ **2** and **4a**. (iii) Mixture of generated **5** with 1-octanol (ROH).



(1)



(2)



(3)

Chlorination of tertiary alcohols

When tertiary alcohols were used as the substrate, diethyl tartrate **4a** was not necessary when the $GaCl_3$ catalyst was used (Table 3, entries 1–3). These reactions proceeded *via* a mechanism different from that shown in Schemes 1 and 2, as H_2 generation was not observed during the reaction. The reaction probably proceeded through an S_N1-type chloro-dehydroxylation with the assistance of a $GaCl_3$ as a Lewis acid, as has been reported for the same type of reaction using $BiCl_3$.[9] However, certain tertiary alcohols that would not be good substrates for S_N1-type reactions showed low chloride product yields (entries 4 and 6). In fact, $BiCl_3$-catalyzed reactions of **1l** and **1m** with **2** for 3 h resulted in low yields (19% and 0%), respectively,[9] probably due to destabilization of the tertiary carbocation either by steric or electronic effects. Interestingly, the $GaCl_3$/tartrate system significantly improved chlorination of **1l** and **1m**, resulting in satisfactory yields (entries 5 and 7). In this case, generation of H_2 was observed. Thus, it was concluded that the reaction proceeds *via* the mechanism shown in Scheme 2. The $GaCl_3$/tartrate system can be applied to chlorination of variety of tertiary alcohols.

Conclusions

In summary, the combination of $GaCl_3$ and diethyl tartrate effectively catalyzed the chlorination of secondary alcohols. Tertiary alcohols that give destabilized carbocations can also be chlorinated using this combined catalyst system. With this system, we have developed a completely catalytic reaction for the chlorination of alcohols under neutral conditions.

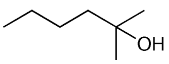
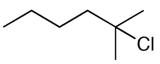
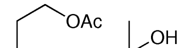
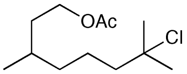
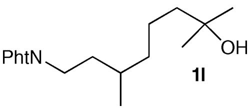
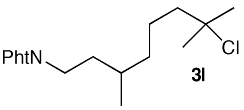
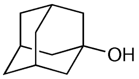
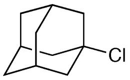
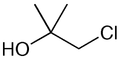
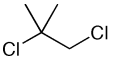
Experimental

IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained with a 400, 100, and 78.7 MHz spectrometer, respectively, with TMS as internal standard. Mass spectra were recorded on a JEOL JMS-DS303 spectrometer. All reactions were carried out under nitrogen. GLC analyses were performed on a Shimadzu GC-14A with FID using a 15 m × 3 mm capillary column packed with TC-WAX, TC-5, or TC-1701 (0.25 μm). Column chromatography was performed on silica gel (MERK C60). Bulb-to-bulb distillation (Kugelrohr) was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Yields were determined by GLC or ^1H NMR using internal standards.

General procedure for chlorination of alcohols catalyzed by the $GaCl_3$/tartrate system (Table 2)

To a solution of (+)-diethyl tartrate (0.1 mmol) in CH_2Cl_2 (1 mL) were added $GaCl_3$ in pentane (0.5 M, 0.1 mL, 0.05 mmol), alcohol **1** (1.0 mmol), and $HSiMe_2Cl$ **2** (1.3 mmol) under nitrogen. The

Table 3 Chlorination of tertiary alcohols **1**[a]

Entry	Alcohol	Time/h	Product	Yield (%)
1	 **1j**	1.5	 **3j**	99
2	 **1k**	2	 **3k**	99
3	 **1l**	3	 **3l**	99
4 5[b]	 **1m**	3 3	 **3m**	6 65
6 7[b]	 **1n**	2 2	 **3n**	16[c] 89[c]

[a] All entries were carried out at room temperature in CH_2Cl_2 with 1.0 equiv of alcohol **1**, 1.3 equiv of $HSiMe_2Cl$ **2**, and 5 mol% of $GaCl_3$. [b] (+)-DET (10 mol%) **4a** was added. [c] Direct observation of the product by NMR because of the high volatility of **3n**.

reaction mixture was stirred under the conditions noted in text. H_2 gas was generated for the first *ca.* 15 minutes. The mixture was quenched by addition of water (10 mL) and extracted with diethyl ether (3 × 10 mL). The collected organic layer was dried over $MgSO_4$ and concentrated *in vacuo*.

General procedure for chlorination of alcohols catalyzed by the $GaCl_3$ system (Table 3)

To a solution of $GaCl_3$ (0.5 M in pentane, 0.1 mL, 0.05 mmol) in CH_2Cl_2 (1 mL) were added alcohol **1** (1.0 mmol) and $HSiMe_2Cl$ **2** (1.3 mmol) under nitrogen. The reaction mixture was stirred under the conditions noted in the text. The mixture was quenched by addition of water (10 mL) and extracted with diethyl ether (3 × 10 mL). The collected organic layer was dried over $MgSO_4$ and concentrated *in vacuo*.

Product data

The spectral data of **3a**,[13] **3b**,[14] **3d**,[2a] **3e**,[2a] and **3k**[12] were in an excellent agreement with the reported data. The spectral data of **3c**, **3f**, **3m**, and **3n** were in an excellent agreement with those of commercially available products.

12-Chlorotetradecyl acetate (3g). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1g**, $GaCl_3$ and (+)-diethyl tartrate in dichloromethane to give the product as a colorless liquid after chromatography (hexane–EtOAc, 97 : 3). Further purification was performed by distillation under reduced pressure, to give the product (including some rearrangement products): bp. 165 °C/0.4 mmHg; IR: (neat) 2927 (C–H), 1743 (C=O), 1242 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.05 (t, J = 6.8 Hz, 2H, 1-H_2), 3.85 (m, 1H, 12-H), 2.05 (s, 3H, $COCH_3$), 1.03 (t, J = 7.4 Hz, 3H, 14-H_3) (other signals could not be identified due to overlap with those of rearrangement by-products); ^{13}C NMR: (100 MHz, $CDCl_3$) 171.3 (C, CO), 65.9 (CH, C-12), 64.5 (CH_2, C-1), 31.5 (CH_2, C-13), 10.9 (CH_3, C-14) (other signals could not be identified due to overlap with those of rearrangement by-products); MS: (CI, 200 eV) *m/z* 293 (M^+ + 3, 31), 291 (M^+ + 1, 100), 255 (M^+ + 1 − HCl, 65), 195 (M^+ + 1 − HCl − CH_3COOH, 47); HRMS: (CI, 200 eV) calcd for $C_{16}H_{32}ClO_2$ 291.2091 found *m/z* 291.2086 (M^+ + 1). Anal. Calcd for $C_{16}H_{31}ClO_2$: C, 66.07; H, 10.74. Found: C, 66.36; H, 10.59.

12-Chloro-1-tridecanol (3h). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1h**, $GaCl_3$ and (+)-diethyl tartrate in dichloromethane to give the product as a colorless liquid after chromatography (hexane–EtOAc, 90 : 10). Further purification was performed by distillation under reduced pressure and GPC, to give the product (including some rearrangement products): bp. 175 °C/0.5 mmHg; IR: (neat) 3309 (OH) cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 4.02 (tq, J = 6.6, 6.6 Hz, 1H, 12-H), 1.50 (d, J = 6.6 Hz, 3H, 13-H_3) (other signals could not be identified due to overlap with those of rearrangement by-products); ^{13}C NMR: (100 MHz, $CDCl_3$) 63.1 (CH_2, C-1), 59.0 (CH, C-12), 40.4 (CH_2, C-11), 25.7 (CH_3, C-13) (other signals could not be identified due to overlap with those of rearrangement by-products); MS: (CI, 200 eV) *m/z* 237 (M^+ + 3, 3.47), 235 (M^+ + 1, 12.3), 217 (M^+ + 1 − H_2O, 41.0), 199 (M^+ + 1 − HCl, 100), 181 (M^+ + 1 − HCl − H_2O, 22.1), 125 (24.0), 111 (26.6), 97 (21.1); HRMS: (CI, 200 eV) calcd for $C_{13}H_{28}ClO$ 235.1829 found *m/z* 235.1822 (M^+ + 1). Anal. Calcd for $C_{13}H_{27}ClO$: C, 66.50; H, 11.59. Found: C, 66.42; H, 11.44.

2-(4-Chloropentyl)isoindole-1,3-dione (3i). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1i**, $GaCl_3$ and (+)-diethyl tartrate in dichloromethane to give the product as a colorless liquid after chromatography (hexane–EtOAc, 80 : 20); further purification was performed by distillation under reduced pressure: bp. 175 °C/1.0 mmHg; IR: (neat) 1774, 1712 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.85 (dd, J = 5.4, 3.2 Hz, 2H, 5-H and 8-H), 7.73 (dd, J = 5.4, 3.2 Hz, 2H, 6-H and 7-H), 4.08 (tq, J = 6.8, 6.8 Hz, 1H, 4′-H), 3.72 (t, J = 6.8 Hz, 2H, 1′-H_2), 1.92 (m, 1H, 3′-H^A), 1.87–1.72 (m, 3H, 3′-H^B and 2′-H_2), 1.50 (d, J = 6.8 Hz, 3H, 5′-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.4 (s, C-1 and C-3), 134.0 (d, C-6 and C-7), 132.0 (s, C-4 and C-9), 123.2 (d, C-5 and C-8), 57.9 (d, C-7′), 37.3 (d, C-1′), 37.3 (d, C-3′), 25.9 (t, C-2′), 25.4 (q, C-5′); MS: (EI, 70 eV) *m/z* 253 (M^+ + 2, 0.82), 251 (M^+, 2.5), 160 (M^+ − $CH_2CH_2CHClCH_3$, 100); HRMS: (EI, 70 eV) calcd for $C_{13}H_{14}ClNO_2$ 251.0709 found *m/z* 251.0713 (M^+). Anal. Calcd for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61; N, 5.56. Found: C, 61.74; H, 5.49; N, 5.60.

2-Chloro-2-methylhexane (3j). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1j** and $GaCl_3$ in dichloromethane to give the product as a colorless liquid after chromatography (hexane–EtOAc, 90 : 10); further purification was performed by distillation under reduced pressure: bp. 58 °C/50 mmHg; IR: (neat) 2962, 1466 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 1.74 (m, 2H, 3-H_2), 1.57 (s, 3H, 1-H_3 or 2-Me), 1.57 (s, 3H, 2-Me or 1-H_3), 1.46 (m, 2H, 4-H_2), 1.33 (tq, J = 7.4, 7.4 Hz, 2H, 5-H_2), 0.93 (t, J = 7.4 Hz, 3H, 6-H_3); ^{13}C NMR: (100 MHz, $CDCl_3$) 71.3 (s, C-2), 45.8 (t, C-3), 32.4 (q, C-1 and 2-Me), 27.3 (t, C-4), 22.8 (t, C-5), 14.0 (q, C-6); MS: (EI, 70 eV) *m/z* 121 (M^+ + 2 − CH_3, 0.75), 119 (M^+ − CH_3, 2.2), 99 (M^+ − Cl, 17), 77 ($C(CH_3)_2Cl$, 65), 56 (100), 41 (55); HRMS: (EI, 70 eV) calcd for $C_6H_{12}Cl$ 119.0628 found *m/z* 119.0630 (M^+ − CH_3). Anal. Calcd for $C_7H_{15}Cl$: C, 62.44; H, 11.23. Found: C, 62.59; H, 11.05.

2-(7-Chloro-3,7-dimethyloctyl)isoindole-1,3-dione (3l). According to the general procedure, this compound was prepared from $HSiMe_2Cl$, **1l** and $GaCl_3$ in dichloromethane to give the product as a solid after recrystallization (hexane–ether): mp. 88–90 °C; IR: (KBr) 1770, 1712 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.84 (dd, J = 5.6, 3.2 Hz, 2H, 5-H and 8-H), 7.71 (dd, J = 5.6, 3.2 Hz, 2H, 6-H and 7-H), 3.71 (m, 2H, 1′-H_2), 1.70 (m, 3H), 1.56 (s, 6H, 8′-H_3 and 7′-Me), 1.59–1.21 (m, 5H), 1.21 (m, 1H), 0.99 (d, J = 6.3 Hz, 3H, 3′-Me); ^{13}C NMR: (100 MHz, $CDCl_3$) 168.4 (C, C-1 and C-3), 133.8 (CH, C-6 and C-7), 132.2 (C, C-4 and C-9), 123.1 (CH, C-5 and C-8), 71.2 (C, C-7′), 46.2 (CH_2), 36.7 (CH_2), 36.2 (CH_2), 35.5 (CH_2), 32.4 (CH_3, 7′-Me), 32.4 (CH_3, C-8′), 30.6 (CH, C-3′), 22.3 (CH_2), 19.3 (CH_3, 3′–Me); MS: (EI, 70 eV) *m/z* 323 (M^+ + 2, 2.41), 321 (M^+, 6.94), 200 (23.0), 161 (47.2), 160 ($PhthNCH_2$, 100), 148 (28.2); HRMS: (EI, 70 eV) calcd for $C_{18}H_{24}ClNO_2$ 321.1496 found *m/z* 321.1502 (M^+). Anal. Calcd for $C_{18}H_{24}ClNO_2$: C, 67.17; H, 7.52; N, 4.35. Found: C, 67.15; H, 7.38; N, 4.47.

Acknowledgements

Financial support from a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, is gratefully acknowledged.

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