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Article

$InCl_3$/NaClO: A Reagent for Allylic Chlorination of Terminal Olefins

Diego S. Pisoni, Douglas Gamba, Carlos V. Fonseca, Jessie S. da Costa, Cesar L. Petzhold, Eduardo R. de Oliveira and Marco A. Ceschi*

Instituto de Química, Universidade Federal do Rio Grande do Sul, CP 15003, 91501-970 Porto Alegre-RS, Brazil

Tricloreto de índio na presença de hipoclorito de sódio promove a cloração alílica de olefinas terminais em meio bifásico (diclorometano/água) com bons rendimentos. Para estabelecer um procedimento geral, escolheu-se a carvona como composto modelo e otimizou-se a estequiometria, temperatura, e tempo de conversão para o respectivo cloreto alílico. Tratando-se β-pineno com tricloreto de índio/hipoclorito de sódio obteve-se seletivamente o cloreto perílico, um precursor importante para a obtenção de derivados de limoneno oxigenados no carbono C-7.

Indium trichloride promotes the chlorination of terminal olefins in the presence of sodium hypochlorite with good results. Carvone was chosen as a model compound to examine some of the general features of this reaction, such as stoichiometry, temperature, reaction time and product conversion. Treatment of β-pinene with sodium hypochlorite in the presence of indium trichloride resulted in a facile rearrangement to selectively yield perillyl chloride, which is an important precursor for C-7 oxygenated limonenes.

Keywords: allylic chlorination, indium trichloride, sodium hypochorite

Introduction

Allylic chlorides are versatile starting materials that are widely used in synthetic organic chemistry, as further manipulation of the chloride may lead to other functional groups and a desired functionalization for the synthesis of natural products.[1-6] These compounds are usually prepared from the corresponding allylic alcohols by the action of a variety of reagents, such as hydrochloric acid,[7] thionyl chloride,[8] titanium (IV) chloride,[9] *N*-chlorosuccinimide,[10] methanesulfonyl chloride/lithium chloride,[11] or chloromethylsilanes.[12] Allylic chlorination is a convenient alternative method of terminal olefin functionalization. Isopropenyl group chlorination can be performed directly by bubbling molecular chlorine through the reaction medium,[13] but this procedure is limited by the difficulty of handling chlorine gas. A feasible procedure for this purpose was reported by Wolinsky and co-workers, using solid CO_2 and calcium hypochlorite.[14,15] As an alternative, Li and co-workers employed a combination of the Vilsmeier reagent and H_2O_2 in the synthesis of eudesmane acids, but the presence of $POCl_3$ excludes the use of acid-sensitive substrates.[16] Recently, Massanet and co-workers, described the preparation of allylic chlorides by reaction of terminal olefins with sodium hypochlorite in the presence of cerium trichloride heptahydrate as an ene-type reaction. The main advantage of this method is in its technical simplicity and safety.[13]

Indium salts have some interesting features, because of their low environmental impact, high chemoselectivity, and tolerance of aqueous media. We now report that $InCl_3$/NaClO in a two-phase system (dichloromethane/water), effectively promotes the allylic chlorination of terminal olefins (Figure 1).

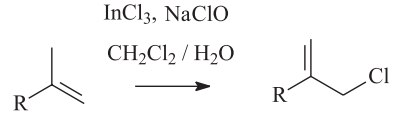


Figure 1. Allylic chlorination of terminal olefins promoted by indium trichloride.

Results and Discussion

The assessment of the scope and limitations of this reaction was made using carvone (**1**) as the substrate (Scheme 1), the aim being to simplify the procedures and to examine some of the general features of this reaction such as stoichiometry, temperature, and product conversion. Use of carvone, allowed us to compare and evaluate the results with the combinations $InCl_3$/NaClO and the related method

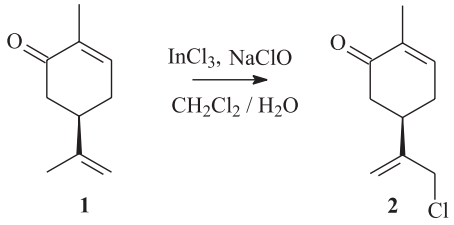
* e-mail: mceschi@iq.ufrgs.br

Table 1. Comparison of carvone chlorination with $InCl_3$/NaClO and $CeCl_3.7H_2O$/NaClO

entry	Lewis acid (equiv.)	NaOCl (equiv.)[a]	Yield (%)[b,c]
1	$InCl_3$ (0.3)	4	0
	$CeCl_3.7H_2O$ (0.3)	4	0
2	$InCl_3$ (0.5)	4	17
	$CeCl_3.7H_2O$ (0.5)	4	10
3	$InCl_3$ (1.1)	2	81
	$CeCl_3.7H_2O$ (1.1)	2	78
4	$InCl_3$ (2.0)	4	Complex mixture
	$CeCl_3.7H_2O$ (2.0)	4	Complex mixture
5	$InCl_3$ (1.1)	4	93
	$CeCl_3.7H_2O$ (1.1)	4	93

[a]Diluted NaClO (5.84% available chlorine); [b]Determined by CG analysis of the crude reaction products with biphenyl as internal standard; [c]Reactions were carried out for 30 min at 0 °C.

using $CeCl_3.7H_2O$ as Lewis acid.[13] The results are summarized in Table 1. The best yield for carvone chlorination (entry 5) was achieved with 1.1 equiv. of $InCl_3$ or $CeCl_3.7H_2O$ and 4.0 equiv. of NaClO. In our trials to reproduce the previously reported procedure,[13] using 2 or 3 equiv. of $CeCl_3.7H_2O$ at room temperature with both solutions, NaClO 5.84% or 13.0%, only a complex mixture of products was observed.



Scheme 1.

A variety of terminal olefins were treated with NaClO in the presence of $InCl_3$ under the optimized carvone chlorination reaction conditions depicted in scheme 1 (entry 5), to give the corresponding chlorinated products in good to excellent yields (Table 2). In all cases, the reactions proceeded smoothly in a two-phase system (dichloromethane/water) at 0 °C for 30 min, loading 1.1 equiv. of $InCl_3$ and excess of NaClO (solution 5.84%). Dihydrocarvone (**3**) (entry 1), limonene oxide (**5**) (entry 2) and cyanohydrin derivative **7** (entry 3) show very high conversion to the chlorinated products. It is interesting to note that the TMS ether functionality in cyanohydrin **7** was not affected by the reaction conditions, and the chlorination of the isopropenyl group was observed. Entries 4-7 show, respectively, the quantitative conversion of octalone **9** (entry 4), α-cyperone (**11**) (entry 5), and the related eudesmane-type sesquiterpene derivatives **13** (entry 6) and **15** (entry 7) to the corresponding chlorinated products **10**, **12**, **14** and **16**.

Octalone **9** and α-Cyperone (**11**) were prepared by alkylation of (*5R*)-dihydrocarvone *via* its chiral imine, using ethyl and methyl vinylketones respectively as electrophiles.[17,18] The *cis*-fused ketol **15** was obtained by the mild aldol cyclization of the diketone epimeric at the angular methyl site (isomer of diketone leading to α-cyperone **11**).[18,19] This ketol exhibits an *equatorial* C4-*methyl* group and a non-stereoidal conformation of the bicyclo[4.4.0]decanone, thus preventing the dehydration step even under mild basic conditions.[19] Alcohol **13** was prepared in two steps from **11,** by lithium/ammonia reduction, followed by the reduction of the resulting *trans*-fused decalone with $LiAlH_4$.[20,21] Both C3-hydroxy and C4-methyl groups in **13** are in an *equatorial* configuration.[19]

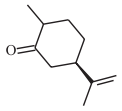
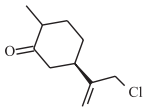
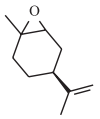
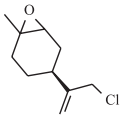
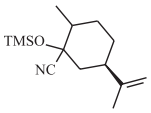
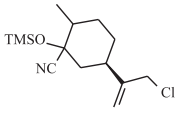
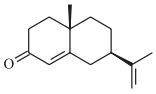
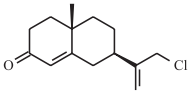
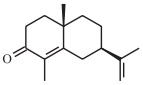
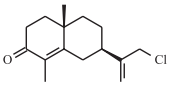
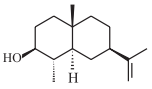
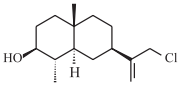
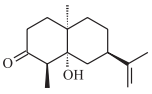
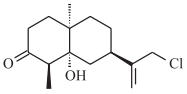
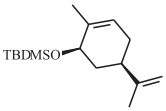
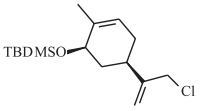
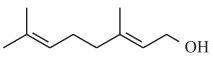
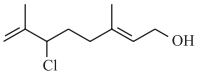
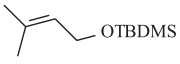
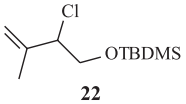
In the case of hydroxylated substrates **13** and **15**, the yields were quantitative as long as the hydroxyl group is distal and not allowed to interfere with the incipient carbocation. Such behavior has been observed previously in the chlorination of olefin substrates bearing a proximal hydroxyl group, with sodium hypochlorite in the presence of cerium trichloride heptahydrate.[13] When *cis*-carveol was subjected to chlorination reaction only a complex mixture was observed. On the other hand, its TBDMS ether **17** was converted to the chlorinated product **18** in 35% yield (entry 8).

Under similar reaction conditions, geraniol **19** (entry 9) and 2-methylallyloxysilane **21**, as examples of non-terminal olefins, afforded the chlorinated product **20** and **22** in 40% and 64% of yield respectively.

Next, we examined the selective rearrangement of β-pinene (**23**) to chlorolimonene derivatives **24** and/or **25** mediated by $InCl_3$/NaClO and compared the outcome with that of the rearrangement mediated by $CeCl_3.7H_2O$/NaClO (Scheme 2). In view of the similarities observed in the behavior of both systems, we initially examined the general procedure outlined by Massanet and co-workers to perform the conversion of b-pinene to perillyl chloride by using $CeCl_3.7H_2O$/NaClO system.[13] However, under the conditions described in the original paper, using $CeCl_3.7H_2O$ (2 equiv.), NaClO solution 13.0% (2 equiv.) in a mixture of CH_2Cl_2/H_2O (1:1 v/v) as solvent, and without temperature determination, we could not reproduce the result described and a complex mixture of products was invariably obtained after several trials. We therefore investigated the feasibility of this approach by setting the appropriate reaction conditions outlined by Massanet protocol.

As depicted in Table 3, the monochlorinated product **24** was obtained in 57% yield using 1.0 equiv. of $InCl_3$, 8.0 equiv. of NaClO (solution 5.84%) and 8.5 h reaction at 0 °C (entry 3). Using $CeCl_3.7H_2O$ under similar reaction conditions, the product **24** was obtained in 35% yield

Table 2. Chlorination of olefins in the presence of NaClO and $InCl_3$

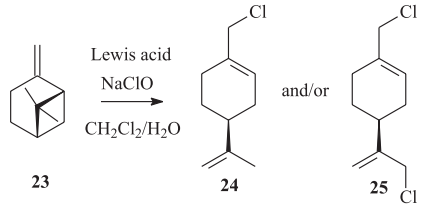
entry	Substrate	Product	$[a]_D$ (concentration)	Yield (%)
1	 **3**	 **4**	+11 (1.70)	95
2	 **5**	 **6**	-47 (1.64)	91
3	 **7**	 **8**		90
4	 **9**	 **10**	+68 (0.83)	70
5	 **11**	 **12**	+89 (1.25)	76
6	 **13**	 **14**	-7 (2.20)	60
7	 **15**	 **16**	+51 (1.13)	58
8	 **17**	 **18**	-33 (1.98)	35
9	 **19**	 **20**		40
10	 **21**	 **22**		64

[a] Yields of pure isolated products; [b] Products were characterized by IR, ^1H and ^{13}C NMR, MS spectroscopic data.

(entry 4) and a larger amount of starting material was observed. In both cases, the dichlorinated product **25** was not observed. It is interesting to note that lower yields were observed after longer reaction time, probably because of the hydrolysis of the chlorinated product under the basic reaction conditions. Also noteworthy is the critical stoichiometry dependence of the Lewis acid that was observed for this pinene rearrangement. Small increase of the Lewis acid amount was also found to afford lower yields of **24**, as depicted in entries 7 and 8.

Surprisingly, the reaction was found to be completed in 10 min at 0 °C using 8 equiv. of NaClO (solution 13.0%) and 1.0 equivalents of Lewis acid, selectively affording the monochlorinated product **24**, in 50% yield with $InCl_3$ and 18% yield with $CeCl_3.7H_2O$ (entries 13 and 14). It was observed that a small increase of the Lewis acid led to improved yield of **24** (71% yield with $InCl_3$ and 47% yield with $CeCl_3.7H_2O$) in a shorter reaction time (entries 15 and 16).

The selective conversion of β-pinene (**23**) to the dichlorinated product **25** was achieved using similar reaction conditions, in a longer reaction time (entries 11 and 12).



Scheme 2.

Conclusions

In conclusion, the combination of sodium hypochlorite in the presence of one equivalent of indium (III) chloride provides a simple method for the preparation of allylic chlorides from olefins. Noteworthy advantages of this method are the safety of the procedure, high product yields, and mild reaction conditions. In addition, an efficient and selective rearrangement of β-pinene to perillyl chloride was achieved. These consideration lead us to believe that this method may represent a valuable alternative to the existing procedures reported in the literature.

Experimental

Melting points were measured on an Electrothermal IA 9100 digital melting point apparatus. IR spectra were measured on a Mattson Galaxy Series FT-IR 3000 (model 3020). ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-200. Chemical shifts are expressed as δ (ppm) relative to TMS as an internal standard and *J* standard values are given in Hz. The products were analyzed by GC on a Shimadzu GC-17A Gas Chromatograph, equipped with a FID detector. GC parameters for achiral analysis: injector 230 °C; detector 300 °C; oven 80 °C for 5 min then 15 °C min^{-1} for 5 min to 300 °C; column pressure 20 kPa, column flow 6.3 mL min^{-1}; linear velocity 53.1 cm s^{-1}; total flow 138 mL min^{-1}; split ratio 1:20; column DB1 15 m × 0.53 mm (internal diameter). Optical rotations were measured in a Perkin-Elmer 341 polarimeter with a 0.1 dm cell at a temperature of 20 °C. HRESIMS data were obtained on a Q-TOF Autospec-Micromass equipment using CH_3CN : H_2O (1 : 1) + HCOOH 0.1% (v/v). HREIMS data were obtained on a VG Autospec spectrometer. Purification by column chromatography was carried out on silica gel 60 (70-230 mesh). Analytical thin-layer chromatography (TLC) was

Table 3. Selective synthesis of (-)-perillyl cloride (**24**) from β-pinene mediated by $InCl_3$ and $CeCl_3.7H_2O$

entry	Lewis acid / equiv.	equiv.of NaOCl[a,b]	time	Product (yield,%)[c, d]
1	$InCl_3$ (2.0)	2b	0.5h	Complex mixture
2	$CeCl_3.7H_2O$ (2.0)	2b	0.5h	**25** (31)
3	$InCl_3$ (1.0)	8a	8.5h	**24** (57)
4	$CeCl_3.7H_2O$ (1.0)	8a	8.5h	**24** (35)
5	$InCl_3$ (1.0)	8a	12.4h	**24** (38)
6	$CeCl_3.7H_2O$ (1.0)	8a	12.4h	**24** (31)
7	$InCl_3$ (1.1)	8a	4.5h	**24** (33)
8	$CeCl_3.7H_2O$ (1.1)	8a	4.5h	**24** (27)
9	$InCl_3$ (0.5)	4b	15 min	**24** (39)
10	$CeCl_3.7H_2O$(0.5)	4b	15 min	**24** (48)
11	$InCl_3$ (1.0)	8b	2h	**25** (59)
12	$CeCl_3.7H_2O$ (1.0)	8b	2h	**25** (53)
13	$InCl_3$ (1.0)	8b	10 min	**24** (50)
14	$CeCl_3.7H_2O$ (1.0)	8b	10 min	**24** (18)
15	$InCl_3$ (1.1)	8b	5 min	**24** (71)
16	$CeCl_3.7H_2O$ (1.1)	8b	5 min	**24** (47)

[a] Diluted NaClO (5.8% available chlorine); [b]Diluted NaClO (13.0% available chlorine); [c]Conversion determined by capillary CG analysis of the crude reaction products with biphenyl as internal standard; [d] Reactions perfomed at 0 °C, except for entry 1 perfomed at 25 °C.

conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254.

General procedure

Alkene (0.5 mmol) in 2.5 mL of CH_2Cl_2 was added to a vigorously stirred solution of $InCl_3$ (121.7 mg, 0.55 mmol) in water, cooled externally with an ice bath. To the resulting mixture was added 2 mmol (2.5 mL) of diluted NaClO (5.84% m/v) and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched by the slow addition of saturated aqueous Na_2SO_3. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 8 mL). The combined organic layers was dried over anhydrous sodium sulfate, and concentrated *in vacuo* and the chlorinated product was purified by column chromatography. The purity of the chlorinated products was checked by GC, and characterization involved NMR (^{1}H and ^{13}C) spectroscopy and mass spectrometry; in many cases spectral data were compared with that reported in the literature. The Yields in Table 1 refer to isolated, analytically pure compounds.

For compounds *(5R)*-5-[1-(chloromethyl)vinyl]-2-methylcyclohex-2-en-1-one (**2**), *(5R)*-5-[1-(chloromethy) vinyl])-2-methylcyclohexanone (**4**), *(4S)*-4-[1-(chloromethyl) vinyl]-1-methyl-7-oxabicyclo[4.1.0]heptane (**6**), IR and NMR data were in agreement with those reported in the literature:[15,22] Optical rotation for compounds: **2** $[\alpha]_D$ -54 (1.84, $CHCl_3$); compound **4** $[\alpha]_D$ +11 (1.70), Lit.[22] $[\alpha]_D$ +6.11 (0.65, $CHCl_3$); compond **6** $[\alpha]_D$ -47 (1.64, $CHCl_3$).

*(1RS, 2RS, 5R)-5-[1-(Chloromethyl)vinyl]-2-methyl-1-trimethylsilanyloxy-cyclohexanecarbonitrile, (**8**)*

IR (film) ν_{max}/cm^{-1}: 2962, 2855, 2361, 1641, 1454, 1253, 1118, 1025, 845, 754 ; ^{1}H NMR (200 MHz) δ 0.25 (s, 9H), 1.01 (d, *J* 6.4Hz, 3H), 1.20-2.0 (m, 6H), 2.25-2.35 (m, 1H), 2.40-2.60 (m, 1H), 4.07 (s, 2H), 5.02 (s, 1H), 5.22 (s 1H); ^{13}C NMR (50 MHz) δ 1.4, 16.1, 31.1, 38.1, 38.7, 42.8, 44.7, 47.2, 75.8, 114.4, 119.8, 147.6 (signals reported for the major diastereomer); EI-MS (70eV), *m/z* (%) [M$^+$, 285-15 (23.9)], 250 (21.6), 243 (54.8), 133 (87.7), 73 (100); HREIMS *m/z* [M$^+$] found: 285.13006; Calc. for $C_{14}H_{24}ClNOSi$: 285.13157.

*(1R, 5R- tert-Butyl-[5-(1-chloromethylvinyl)-2-methyl cyclohex-2-enyloxy]-dimethylsilane, (**18**)*

$[\alpha]_D$ -33 (1.98, $CHCl_3$); IR (film) ν_{max}/cm^{-1}: 2953, 2929, 2856, 1647, 1467, 1253, 1093, 835, 775 ; ^{1}H NMR (200 MHz) δ 0.08 (s, 6H), 0.89 (s, 9H), 1.39-2.20 (m, 4H), 1.68 (s, 3H), 2.48 (m,1H), 4.06 (s, 2H), 4.25 (br, 1H), 4.90 (s,1H), 5.15 (s, 1H), 5.42 (br,1H); ^{13}C NMR (50 MHz) δ -4.8, 18.1, 19.7, 25.9, 31.5, 31.5, 36.2, 38.5, 47.5, 71.3, 113.5, 122.7, 137.3, 148.6; HREIMS *m/z* [M$^+$] found: 300.16084; Calc. for $C_{16}H_{29}ClOSi$: 300.16762.

*(6R,9R)-12-Chloro-9-isopropenyl-6-methylbicyclo[4.4.0] dec-1-en-3-one, (**10**)*

$[\alpha]_D$ +68 (0.83, $CHCl_3$); IR (film) ν_{max}/cm^{-1}: 2927, 2852, 1672, 1616, 1451, 1245, 930, 749 ; ^{1}H NMR (200 MHz) δ 1.25 (s, 3H), 1.35-2 (m, 6H), 2.2-2.6 (m, 5H), 4.1 (s,2H), 5.06 (s, 1H), 5.22 (s, 1H), 5.76 (s, 1H); ^{13}C NMR (50 MHz) δ 22.1, 27.7, 34.0, 35.5, 37.7, 38.0, 41.2, 41.6, 47.3, 114.1, 124.9, 148.3, 168.8, 199.6; EI-MS (70eV), *m/z* (%) [M$^+$, 238 (33.9)], 203 (38.6), 175 (90.1), 91 (100.0), 79 (93.8); HREIMS *m/z* [M$^+$] found: 238.11564; Calc. for $C_{14}H_{19}ClO$: 238.11244.

*(4aS,7R)-7-[1-(chloromethyl)vinyl]-1,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphtha-len -2(3H)-one, (**12**)*

$[\alpha]_D$ +89 (1.25 $CHCl_3$); lit.[16] $[\alpha]_D$ +96.0; IR and ^{1}H NMR data were in agreement with those reported in the literature. Complementary data ^{13}C NMR (50 MHz) δ 10.9, 22.4, 27.3, 33.2, 33.7, 35.8, 37.3, 41.3, 41.8, 47.6, 113.9, 129.1, 148.8, 161.1, 199.0; EI-MS (70eV), *m/z* (%) [M$^+$, 252 (77.4)], 217 (55.8), 136 (93.8), 91 (100).

(1S,2S,4aS,7R,8aS)-7-[1-(chloromethyl)vinyl]-1,4a-dimethyldecahydronaphthalen-2-ol, (14)

$[\alpha]_D$ -7 (2.20, $CHCl_3$: IR (film) ν_{max}/cm^{-1}: 3348, 2929, 1639, 1024, 906, 748 : ^{1}H NMR (200 MHz) δ 0.87 (s, 3H), 0.97 (d, *J* 6.2 Hz, 3H), 1.10-2.20 (m, 14H), 3.14 (m, 1H), 4.10 (s, 2H), 5.0 (s, 1H), 5.14 (s, 1H); ^{13}C NMR (50 MHz) δ 14.9, 16.9, 26.9, 29.8, 30.9, 33.2, 39.3, 39.5, 41.4, 41.5, 47.8, 48.8, 76.7, 113.0, 150.1; EI-MS (70eV), *m/z* (%) [M$^+$, 256 (7.5)]; 238 (20.5), 161 (96.7), 121 (84.3), 107 (77.6), 93 (88.7), 81 (87.9), 55 (100);); HRESIMS *m/z* Found: 239.1680; Calc. for: $C_{15}H_{25}Cl$ +H - H_2O: 239.1521.

*(1R,4aR,7R,8aS)-7-[1-(chloromethyl)vinyl]-1,4a-dimethyloctahydronaphthalen-2(1H)-one, (**16**)*

$[\alpha]_D$ +51 (1.13, $CHCl_3$:IR (film) ν_{max}/cm^{-1}: 3348, 2937, 1716, 1008, 935, 742 ; ^{1}H NMR (200 MHz) δ 1.03 (d, *J* 6.6 Hz, 3H), 1.40-2.30 (m, 12H), 2.50 (m,

2H), 3.02 (q, *J* 6.6 Hz, 1H), 4.01 (s, 2H), 5.03 (s, 1H), 5.18 (s,1H); ^{13}C NMR (50 MHz) δ 6.6, 21.6, 26.6, 33.26, 36.6, 37.2, 37.4, 37.9, 46.8, 47.8, 80.8, 113.9, 148.3, 212.2; HRESIMS *m/z* Found: 253.1494; Calc. for $C_{15}H_{23}ClO_2$ + H – H_2O: 253.1314.

*(2E)-6-Chloro-3,7-dimethyl-octa-2,7-dien-1-ol, (**20**)*

IR (film) ν_{max}/cm^{-1}: 3348, 2920, 1658, 1648, 1444, 1378, 1000, 906, 780; ^{1}H NMR (200 MHz) δ 1.68 (s, 3H), 1.81 (s, 3H), 1.80-2.24 (m, 4H), 4.16 (d, *J* 6.8 Hz, 2H), 4.35 (t, *J* 6.5 Hz, 1H), 4,90 (s, 1H), 5.01 (s, 1H); 5.42 (t, *J* 6.8Hz, 1H); ^{13}C NMR (50 MHz) δ 16.3, 17.0, 29.7, 34.5, 36.5, 59.3, 66.2, 114.3, 124.3, 138.0, 144.2 For reported data of IR and ^{1}H NMR, see reference 23; EI-MS (70eV), *m/z* (%) [M$^+$, 192 (3.7)], 157 (9.2), 175 (81.7), 105 (73.6), 91 (100), 79 (94.6).

*tert-Butyl-(2-Chloro-3-methylbut-3-enyloxy)-dimethyl-silane, (**22**)*

IR (film) ν_{max}/cm^{-1}: 3082, 2929, 2858, 1647, 1467, 1255, 1118, 906, 835, 779; ^{1}H NMR (200 MHz) δ 0.04 (s, 6H), 0.86 (s, 9H), 1.78 (s, 3H), 3.76 (d, *J* 6.9 Hz, 2H), 4.35 (t, *J* 6.9 Hz, 1H), 4.94 (s, 1H), 5.04 (s, 1H); ^{13}C NMR (50 MHz) δ -5.37, -5.26, 17.43, 18.28, 25.79, 65.57, 65.63, 115.80, 142.10; HREIMS *m/z* [M$^+$] Found: 234.11171; Calc. For $C_{11}H_{23}ClOSi$: 234.12067.

*(4S)-1-(chloromethyl)-4-isopropenylcyclohexene, (**24**)*

$[\alpha]_D$ -72 (1.78, $CHCl_3$); -52(2.0, CH_3OH), Lit.[24] $[\alpha]_D$ –56 (2.0, MeOH); IR (film) ν_{max}/cm^{-1}: 3082, 2922, 1668, 1643, 1437, 1259, 889, 648; ^{1}H NMR (200 MHz) δ 1.74 (s, 3H), 1.40-2.40 (m, 7H), 4.01 (s, 2H), 4.72 (br, s, 2H), 5.84 (br, s, 1H); IR and NMR data were in agreement with those reported in the literature.[25] EI-MS (70eV), *m/z* (%) [M$^+$, 170 (49.4)], 135 (85.0), 95 (98.5), 91 (100), 79 (77.2).

*(4S)-1-(chloromethyl)-4-[1-(chloromethyl)vinyl] cyclohexene, (**25**)*

$[\alpha]_D$ -66 (1.82, $CHCl_3$); IR (film) ν_{max}/cm^{-1}: 2997, 2921, 2837, 1641, 1269, 910, 748, 688; ^{1}H NMR (200 MHz) δ 1.82-2.1 (m, 2H), 2.15-2.5 (m, 5H), 4.01 (s, 2H), 4.11 (s, 2H), 5.01 (s, 1H), 5.20 (s, 1H), 5.83 (br, 1H); ^{13}C NMR (50 MHz) δ 26.2, 27.5, 31.1, 36.1, 47.7, 49.9, 113.6, 126.5, 134.2, 148.9; EI-MS (70eV), *m/z* (%) [M$^+$, 204 (1.9)], 157 (21.9), 155 (66.7), 119 (33.1), 102 (54,8), 91 (100), 79 (61.8), 67 (94.9); HREIMS *m/z* [M$^+$] Found: 204.04806; Calc. for $C_{10}H_{14}Cl_2$: 204.04725.

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