chromatography (eluted by hexanes only) gave ***cis*-1,1-dimethyl-2,5-diphenylsilacyclopent-3-ene**[5] **(37)** in 66% yield: ^{1}H NMR (200 MHz) δ 7.00–7.30 (m, 10 H), 6.11 (s, 2 H), 3.27 (s, 2 H), 0.39 (s, 3 H), −0.67 (s, 3 H); ^{13}C NMR δ 143.4, 135.0, 128.3, 126.4, 124.3, 39.9, −2.8, −6.8; IR (neat) 3078, 3059, 3020, 2956, 2850, 1599, 1493, 1248, 1061, 858, 802, 746, 698 cm^{-1}; EIMS *m/z* (relative intensity) 264 (M$^{\bullet+}$, 40), 249 (17), 205 (13), 173 (100), 145 (61), 121 (44), 105 (10), 91 (25), 77 (7); HRMS calcd for $C_{18}H_{20}Si$ and $C_{17}{}^{13}CH_{20}Si$ 264.1334 and 264.1368, found 264.1342 and 265.1365.

1,1-Diphenyl-3,4-dimethylsilacyclopent-3-ene[5,27] **(38)**: 65% yield; ^{1}H NMR δ 7.58–7.52 (m, 4 H), 7.42–7.32 (m, 6 H), 1.86 (s, 4 H), 1.77 (s, 6 H); ^{13}C NMR δ 136.4, 134.8, 130.8, 129.4, 127.9, 24.2, 19.4; IR (neat) 3064, 2978, 2895, 2868, 1645, 1587, 1427, 1167, 1115, 731, 698 cm^{-1}; EIMS *m/z* (relative intensity) 264 (M$^{\bullet+}$, 100), 262 (11), 186 (94), 181 (55), 145 (11), 105 (48).

1,1-Diphenyl-3-methylsilacyclopent-3-ene[27] **(39)**: 96% yield; ^{1}H NMR δ 7.64–7.58 (m, 4 H), 7.46–7.37 (m, 6 H), 5.70 (m, 1 H), 1.90 (m, 5 H), 1.83 (m, 2 H); ^{13}C NMR δ 140.1, 136.2, 134.7, 129.4, 127.9, 124.8, 22.6, 21.8, 17.6; IR (neat) 3066, 2999, 2908, 2879, 1637, 1587, 1427, 1155, 1115, 723, 698 cm^{-1}; EIMS *m/z* (relative intensity) 250 (M$^{\bullet+}$, 83), 208 (12), 181 (76), 172 (100), 145 (4), 105 (48).

1,1-Diphenyl-3-(4-methyl-3-pentenyl)silacyclopent-3-ene (40): 91% yield; ^{1}H NMR δ 7.66–7.61 (m, 4 H), 7.48–7.39 (m, 6 H), 5.78 (s, 1 H), 5.20 (s, 1 H), 2.26 (s, 4 H), 1.93 (s, 2 H), 1.86 (s, 2 H), 1.77 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR δ 144.0, 136.3, 134.7, 131.3, 129.4, 127.9, 124.4, 124.2, 36.7, 26.5, 25.7, 19.4, 17.7, 17.3; IR (neat) 3066, 3049, 2999, 2964, 2912, 2883, 1633, 1588, 1427, 1157, 1115, 727, 698, 623 cm^{-1}; EIMS *m/z* (relative intensity) 318 (M$^{\bullet+}$, 8), 275 (12), 249 (38), 240 (75), 207 (33), 171 (100), 145 (15), 105 (39), 69 (68); HRMS calcd for $C_{22}H_{26}Si$ 318.1804, found 318.1809. Anal. Calcd: C, 82.96; H, 8.23. Found: C, 83.16; H, 8.22.

1,1,3-Triphenylsilacyclopent-3-ene[28] **(41)**: 93% yield; ^{1}H NMR δ 7.62–7.15 (m, 15 H), 6.51 (m, 1 H), 2.25 (m, 2 H), 2.08 (m, 2 H); ^{13}C NMR δ 141.8, 140.2, 135.5, 134.7, 129.6, 128.2, 128.0, 127.0, 126.9, 125.7, 18.4, 18.1; IR (neat) 3066, 3049, 3018, 2914, 2879, 1606, 1493, 1427, 1153, 1117, 727, 696 cm^{-1}; EIMS *m/z* (relative intensity) 312 (M$^{\bullet+}$, 100), 234 (95), 156 (28), 105 (50).

Typical Reaction of Unsymmetrical (2-Butene-1,4-diyl)-magnesium with $SiCl_4$. Newly formed **2c**, prepared from isoprene (0.250 g, 3.67 mmol) and excess activated magnesium, in 20 mL of THF was cooled to −78 °C. $SiCl_4$ (0.256 g, 1.50 mmol) was added via a disposable syringe. After being stirred at −78 °C for 1 h, the mixture was gradually warmed to 0 °C and an aqueous solution of 1.5 N HCl (15 mL) was added. The reaction mixture was washed with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 mL), and the combined organic parts were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (15 mL) and dried over anhydrous Na_2SO_4. Evaporation of solvents and flash column chromatography afforded **2,7-dimethyl-5-silaspiro[4.4]nona-2,7-diene**[21] **(42)**: 0.185 g, 75%; ^{1}H NMR 5.53 (m, 2 H), 1.77 (t, *J* = 1.0 Hz, 6 H), 1.48 (d, *J* = 1.1 Hz, 4 H), 1.40 (s, 4 H); ^{13}C NMR δ 140.2, 124.9, 22.6, 21.8, 17.8; IR (neat) 3005, 2958, 2927, 2908, 2879, 2848, 1637, 1448, 1433, 1213, 1161, 1022, 756 cm^{-1}; EIMS *m/z* (relative intensity) 164 (M$^{\bullet+}$, 73), 149 (3), 136 (8), 122 (12), 109 (4), 96 (100).

2,7-Bis(4-methyl-3-pentenyl)-5-silaspiro[4.4]nona-2,7-diene (43): 62% yield; ^{1}H NMR δ 5.55 (s, 2 H), 5.09 (s, 2 H), 2.09 (s, 8 H), 1.67 (s, 6 H), 1.59 (s, 6 H), 1.47 (s, 4 H), 1.40 (s, 4 H); ^{13}C NMR δ 144.2, 131.3, 124.5, 124.1, 36.8, 26.4, 25.7, 19.4, 17.7, 17.3; IR (neat) 3001, 2966, 2912, 2879, 1631, 1448, 1375, 1161, 823, 760; EIMS *m/z* (relative intensity) 300 (M$^{\bullet+}$, 15), 257 (6), 231 (9), 203 (4), 175 (5), 163 (100), 135 (6), 121 (3), 109 (7), 95 (13), 69 (44); HRMS calcd for $C_{20}H_{32}Si$ 300.2273, found 300.2278. Anal. Calcd: C, 79.93; H, 10.73. Found: C, 80.24; H, 11.12.

2,7-Diphenyl-5-silaspiro[4.4]nona-2,7-diene (44): 34% yield; ^{1}H NMR δ 7.55–7.49 (m, 4), 7.36–7.20 (m, 6 H), 6.44 (s, 2 H), 1.96 (s, 4 H), 1.80 (s, 4 H); ^{13}C NMR δ 141.9, 140.4, 128.2, 127.1, 126.8, 125.6, 18.3, 18.2; IR (neat) 3080, 3057, 3020, 2916, 2879, 1604, 1493, 1444, 1159, 997, 767, 742, 694 cm^{-1}; EIMS *m/z* (relative intensity) 288 (M$^{\bullet+}$, 100), 158 (57), 105 (15), 71 (14); HRMS calcd for $C_{20}H_{20}Si$ 288.1334, found 288.1328.

Acknowledgment. The financial support of this work provided by the National Institutes of Health (Grant GM35153) is gratefully acknowledged.

Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra of **10–14, 16, 18, 19, 22, 25–33, 35, 36, 43,** and **44** (28 pages). Ordering information is given on any current masthead page.

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Synthesis of α-Ketols Mediated by Divalent Samarium Compounds

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Received May 29, 1990

Coupling reactions of acid chlorides are mediated by SmI_2 and $SmCp_2$, leading to α-ketols **3**. Condensation reactions of acid chlorides on aldehydes similarly product α-ketols **5**; with ketones, best results are obtained with use of SmI_2. Reactivities of SmI_2 and $SmCp_2$ are compared and mechanisms of the reactions discussed. Formation of an acylsamarium species is shown.

Since our first report in 1977 on an easy preparation of diiodosamarium,[1] many applications of this reagent to organic synthesis have been developed by ourselves and different groups. These reactions are summarized in review articles.[2-5] Most of them are related to Barbier-type reactions[6-11] or to reductive properties of diiodosamarium, such as deoxygenation of epoxides,[6] reduction of alkyl halides,[7,12] or formation of pinacols.[13,14]

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Table I. Formation of Diketones 2, Ketols 3, and Ketol Esters 4 from Acid Chlorides in the Presence of SmX_2

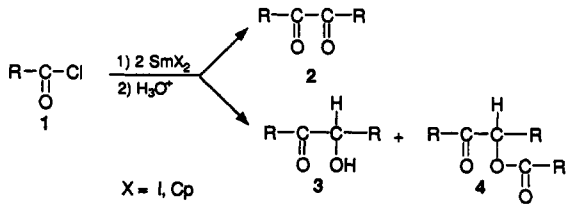
R	X	2	3	4
C_6H_5	I	78[a]		
C_6H_5	Cp	75[a]		
C_8H_{17}	I		75[a]	
$(CH_3)_3CCH_2$	I	20[b]	38[b]	15[b]
$(CH_3)_3CCH_2$	Cp	10[b]	32[b]	30[b]
$Cl(CH_2)_4$	I		20[a]	30[a]
cyclohexyl	I	12[b]	38[a]	10[b]
cyclohexyl	Cp		58[a]	22[b]
1-adamantyl	I		55[a]	
1-adamantyl	Cp		59[a]	

[a] Isolated yield (%), reactions performed in THF with 2.25 equiv of SmX_2 (X = I, room temperature; X = Cp, t (°C) = −20). [b] GC yield (%).

We have described coupling reactions of acid chlorides mediated by SmI_2 leading to α-diketones or α-ketols.[15,16] Synthetic routes to α-ketols using unmasked acyl anions are not numerous; condensation of acyllithium compounds on ketones or aldehydes have been reported.[17,18] Thus, it was interesting to investigate more thoroughly reactions of acid chlorides leading to α-ketols. We previously studied some aspects of the reactivity of $SmCp_2$,[19,20] and now we extend the study of coupling reactions of acid chlorides to this divalent reagent. Reactivities of SmI_2 and $SmCp_2$ are compared, the scope of the reactions is examined, and the mechanisms of the reactions are discussed here.

Results

Reactivities of Acid Chlorides with SmI_2 and $SmCp_2$. SmI_2 has been shown to react with aromatic acid chlorides to give formation of α-diketones in good yields, while with pivaloyl chloride α-ketol has been obtained.[15] Reaction of aliphatic acid chlorides RCOCl with an excess of SmI_2 produces ketones $RCOCH_2R$ through reduction of an intermediate ketolate.[21] We reinvestigated the reactivity of acid chloride with SmI_2 and extended the study to the reactivity with $SmCp_2$ to determine if it is possible to obtain α-diketone or α-ketol according to experimental conditions and nature of substrates.



Results are quoted in Table I. Aromatic acid chlorides lead to α-diketones **2** and aliphatic chlorides mainly to α-ketols **3** with use of SmI_2 as well as $SmCp_2$. Two equivalents of divalent samarium compound are needed to get the α-ketol in good yield. Reactions were run at room temperature with SmI_2 and at −20 °C with $SmCp_2$. Benzil is the unique product of the reaction between benzoyl chloride and $SmCp_2$ or SmI_2 and is isolated in good yield. Phenylacetyl chloride gives at room temperature a decarbonylation reaction with $SmCp_2$, leading to formation of dibenzyl in 85% yield. With SmI_2, this decarbonylation occurs only when it is slowly added to phenylacetyl chloride at room temperature.[16] Aliphatic acid chlorides provide α-ketols mixed with variable amounts of esters **4** of ketols, probably because esterification of samarium ketolate is competitive with obtention of the ketolate. This side reaction can be minimized by slow addition of acid chloride to SmI_2 or $SmCp_2$. α-Diketones are not observed or are formed in small quantities. Even when 1 equiv of SmX_2 reacts with 1 equiv of aliphatic acid chloride, α-diketone is not obtained as the main product contrary to a previous preliminary report.[15]

No difference on the reactivities of SmI_2 and $SmCp_2$ in the coupling reactions of acid chlorides have been noticed; aliphatic chlorides are transformed into α-ketols and aromatic chlorides into α-diketones.

Table II. Formation of Ketols 5 from RCOCl and R^1COR^2 in the Presence of SmX_2

entry	R	R^1, R^2	X	5[a]	3[b]
1	t-Bu	C_6H_{13}, H	Cp[c]	59 (3)	5
2	t-Bu	C_6H_5, H	Cp[c]	65 (4)	3
3	t-Bu	CH_3CH_2, H	I[d]	64	
4	t-Bu	n-C_6H_{13}, CH_3	Cp[c]	0	g
5	1-adamantyl	CH_3CH_2, H	Cp[c]	63 (20)	15
6	1-adamantyl	CH_3CH_2, H	I[d]	50 (13.5)	
7	1-adamantyl	C_6H_5, H	Cp[c]	60	
8	1-adamantyl	CH_3CH_2, H	Cp[d]	60	
9	C_6H_5	CH_3CH_2, H	Cp[c]	0	e
10	C_6H_5	CH_3CH_2, H	Cp[d]	10	g
11	C_6H_5	C_6H_5, H	I[d]	86	
12	cyclohexyl	CH_3CH_2, H	Cp[c]	0	48
13	cyclohexyl	CH_3CH_2, H	Cp[d]	48 (12)	8
14	1-methylcyclohexyl	CH_3CH_2, H	Cp[c]	52 (3)	8
15	1-methylcyclohexyl	CH_3CH_2, H	Cp[d]	32	8[f]
16	1-methylcyclohexyl	CH_3CH_2, H	I[d] (4)	56 (3)	3
17	1-methylcyclohexyl	C_6H_5, H	Cp[c]	43	0
18	n-C_8H_{17}	CH_3CH_2, H	Cp[c]	0	g
19	n-C_8H_{17}	CH_3CH_2, H	Cp[d]	47	0[f]
20	n-C_8H_{17}	$(CH_2)_5$	I[d]	82	0
21	CH_3	$(CH_2)_5$	I[d]	48	

[a] Isolated yield (%; GC% of isomeric ketol **6**). [b] GC yield (%). [c] Two-step procedure; RCOCl, then R^1COR^2 are successively added to $SmCp_2$ in THF; t (°C) = −20; reaction time 0.5 h for addition of RCOCl; total reaction time 2.5 h; $SmCp_2$/RCOCl = 2.5; RCOCl/R^1COR^2 = 1. [d] One-step procedure, RCOCl and R^1COR^2 are mixed and added to $SmCp_2$. [e] $C_6H_5COCOC_6H_5$, 75% isolated yield. [f] About 10% (GC yield) of ketone $RCOCHR^1R^2$ was observed. [g] Complex mixture.

Reactions of Acid Chlorides on Aldehydes or Ketones Promoted by SmI_2 or $SmCp_2$. Condensation of acid chlorides on aldehydes or ketones mediated by SmI_2 utilizing Barbier-type conditions have been previously described.[16] Reactivity of $SmCp_2$ is now compared to that of SmI_2 by use of two different experimental procedures: (i) addition of the mixture of acid chloride and aldehyde or ketone on the divalent samarium compound (Barbier-type procedure) and (ii) sequential addition of acid chloride and of aldehyde or ketone on the samarium derivative.

Results are outlined in Table II. α-Ketols **5** are formed with $SmCp_2$ as with SmI_2, but the yields depend on the structures of acid chlorides and electrophiles and are sometimes lowered by formation of byproducts. α-Ketols **3** generated by homocoupling of the acid chlorides are the main secondary products. In some cases (entries 15, 19), a small amount of ketone $RCOCHR^1R^2$ formed by re-

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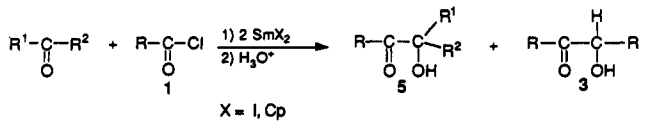
duction of the samarium ketolate that leads to 5 is observed in the crude material.[21]



By use of the Barbier-type procedure with SmI_2 and $SmCp_2$, aliphatic acid chlorides and aliphatic aldehydes (R^1CHO) give good yields of 5. In those cases, α-ketol isomer 6 ($RCHOHCOR^1$) is obtained in mixture with 5 in 0–20% yield. Reactions between aliphatic acid chlorides and aromatic aldehydes give low yields owing to competitive pinacol formation. Benzoyl chloride reacts with aldehydes to give an α-ketol in very poor yields when the reaction is promoted by $SmCp_2$ (entry 10); the main product is benzil. On the contrary, the same reaction with SmI_2 leads to α-ketols 5 in good yields (entry 11).[16] At room temperature, reaction of acid chlorides with ketones mediated by $SmCp_2$ produces α-ketols 5 in low yields, in mixture with the ketols 3 coming from the coupling of the acid chloride. At lower temperature (−20 °C), the ratio of ketol 5 in the reaction mixture is increased. Since good results have been obtained with SmI_2, this reaction has not been developed here.[16]

When a sequential addition of the substrates (acid chloride followed by ketone or aldehyde) is realized on $SmCp_2$, the product of the reaction depends on the substitution of the carbon in the α-position to the carbonyl of the acid chloride. With mono or disubstituted α-carbon, the ketol 3 resulting of the coupling of acid chloride is the sole product (entries 12, 18). With trisubstituted α-carbon, α-ketols 5 resulting from condensation of acid chlorides on all types of aldehydes are obtained in good yields (entries 1,2,5,7,14,17), but the reaction does not work with ketones (entry 4). This sequential procedure was uneffective with SmI_2: only α-ketols 3 arising from coupling of acid chlorides are formed in all cases.

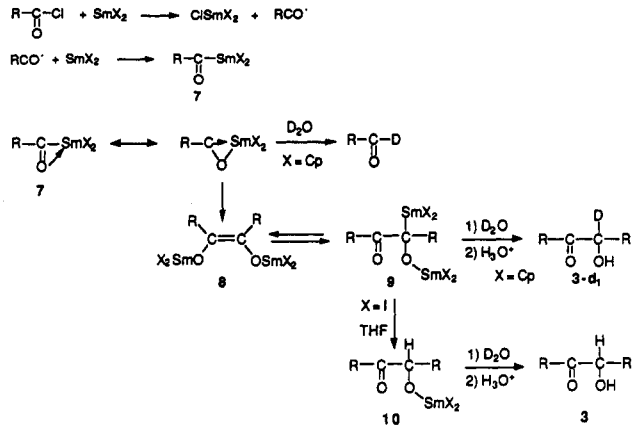
The best experimental conditions to get α-ketols 5 in satisfactory yields depend on the nature of the substrates. SmI_2 should be used to perform reactions between ketones and acid chlorides, but a sequential addition of reagents on $SmCp_2$ is more efficient for reaction of aromatic aldehydes with acid chlorides. In the case of aliphatic aldehydes and acid chlorides, both divalent samarium reagents in Barbier-type conditions or $SmCp_2$ in sequential procedure (acid chloride with trisubstituted α-carbon) give similar results.

Discussion

In the preceding reports concerning reactions of acid chlorides with SmI_2,[15,16] we suggested the transient formation of an acylsamarium species. Reduction of the acid chloride by a first molecule of SmI_2 into an acyl radical would be followed by reduction of this radical by SmI_2 into an organometallic acyl species 7 (Scheme I). Involvement of an acyl radical has been shown in the reactions of some acid chlorides. The double cyclization reaction observed with (allyloxy)benzoic chlorides is well explained by intramolecular addition of an acyl radical on the double bond.[22,23]

By use of $SmCp_2$ and an acid chloride with a tertiary atom in the α-position of the carbonyl at low temperature

Scheme I



(−20 °C), a sequential addition of the acid chloride and of deuterated water allows formation of deuterated aldehyde (isolated yield in RCOD; R = 1-adamantyl (63%), R = 1-methylcyclohexyl (25%)). In the same conditions, addition of the acid chloride followed by that of an aldehyde leads to α-ketol 5. This behavior indicates the formation of an acylsamarium compound. The same intermediate was presumed in the carbonylation reaction of tertiary butyl bromide in presence of $SmCp_2$ at −20 °C followed by addition of an aldehyde.[24] An acyllutetium complex t-$BuCOLuCp_2$ was previously isolated by Evans et al., and its spectroscopic data indicate that its structure is better represented by an oxycarbene structure $Cp_2Lu(\eta^2\text{-}COCMe_3)$.[25] By analogy, we propose to write the samarium compound in two mesomeric forms. We found that the acylsamarium compound 7 is more stable with hindered alkyl groups. This finding is in agreement with usual observations on lanthanides complexes. Some examples of stabilization of complexes through steric grounding of ligands have been reported, for instance, replacement of cyclopentadienyl by pentamethylcyclopentadienyl ligands or by use of bulky alkyl groups.[26,27]

When the acylsamarium intermediate resulting from reaction of 1-adamantanecarboxylic acid chloride on dicyclopentadienylsamarium at −20 °C is allowed to warm to room temperature, α-ketol 3 (R = 1-adamantyl) is obtained within 2 h after hydrolysis. Corresponding ketolate 9 must be the result of the dimerization of the acylsamarium species that behaves as a carbenoid species, leading to enediolate samarium intermediate 8 (Scheme I). Such a dimerization has been observed for bis[(pentamethylcyclopentadienyl)formyl]samarium complexes by Evans.[28] Similarly, carbonylation of phenyllithium or (trimethylsilyl)lithium followed by treatment by acetic anhydride or silylating agent, respectively, leads to the isolation of the cis enediacetate and ene disilyl ether, indicating intermediacy of lithium enediolate.[29,30] Attempts at trapping the transient species 8 have been unsuccessful, probably due to a very rapid isomerization into samarium

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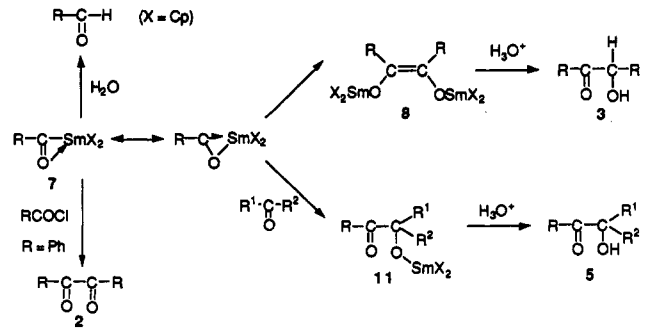
Scheme II



ketolate compound **9**. After deuterolysis of the dicyclopentadienyl ketolate **9** complex prepared by leaving the acylsamarium **7** from −20 °C to room temperature, deuterium is incorporated in the ketol **3** (R = 1-adamantyl). There was no deuterium incorporation at carbon when the samarium ketolate prepared from the same acid chloride and SmI_2 was treated by D_2O. We propose an interpretation based on the cleavage of the samarium–carbon bond of the ketolate **9** by THF leading to species **10**. Such a difference can be explained by a stabilization of the carbon–samarium bond on replacing iodide by cyclopentadienyl ligands. Similar effects have been already noticed in the reaction of benzylic halides with $SmCp_2$.[19] Dicyclopentadienylorganometallic compounds were characterized, while intermediacy of diiodoorganometallic species have never been proved in reaction of alkyl or benzylic halides with SmI_2.

Acylsamarium intermediate **7** reacts with aldehydes, giving samarium ketolate **11**, which after hydrolysis is transformed into α-ketol **5**. The similar results for the reaction of acid chlorides with aldehydes using $SmCp_2$ (sequential procedure) or Barbier-type conditions with $SmCp_2$ or SmI_2 imply involvement of the same acyl species in the three cases. Reaction of acid chlorides on ketones, which gives good yields when mediated by SmI_2, does not occur with use of $SmCp_2$ with a sequential addition of the substrates. This observation is indicative that dicyclopentadienylacylsamarium species are less reactive than diiodosamarium acyl species. Mechanism of formation of α-ketols **3** and **5** is summarized in Scheme II.

Conclusion

Aliphatic acid chlorides are coupled by SmI_2 and $SmCp_2$ to give α-ketols. Coupling of acid chlorides with aldehydes or ketones to α-ketols can also be mediated by these two divalent samarium compounds. SmI_2 is preferably used for ketones, $SmCp_2$ for aromatic aldehydes, and either of the two reagents for aliphatic aldehydes. Acylsamarium species are the key intermediates for these reactions.[31] Our method does not need very low temperatures as in the carbonylation of lithium derivatives[17] and is not restricted to hindered ketones as the recently reported lithium–tellurium exchange.[18] We are currently looking to new aspects of the reactivity of acylsamarium species with the aim to find specific reactions useful in organic synthesis.

Experimental Section

General Procedures. A Bruker AM 200 NMR spectrometer operating at 200 MHz for ^1H and 50.4 MHz for ^{13}C was used for determining spectra with tetramethylsilane as the internal standard in $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane. Infrared spectra were recorded neat and are reported in cm^{-1}. Mass spectra (MS; 70 eV) data were determined on an R-10 gas chromatograph/mass spectrometer. GC analyses were performed with a 25-m BP 1 capillary column connected with a computing integrator.

THF solutions of SmI_2 and $SmCp_2$ in suspension in THF were prepared according to the previously reported procedures.[1,19] Alternatively, commercial solutions of SmI_2 (Strem, Aldrich) were used. Unless otherwise stated, all organic compounds were commercially available and distilled prior to use. 1-Methylcyclohexanecarboxylic acid chloride was obtained from 1-methylcyclohexanecarboxylic acid using the usual procedure.[33] All the reactions were carried out under argon atmosphere. Silica gel 60 (230–400 mesh) was used for flash chromatography.

General Procedure for Synthesis of Ketols 3 with SmI_2. In a typical experiment, 2 mmol of acid chloride dissolved in 10 mL of THF was added within 1 h with use of a syringe pump to a solution of SmI_2 in THF (42 mL; 0.1 N). At the end of the addition, the reaction mixture turns green. It is immediately treated with 0.1 N HCl. Extraction with ether is followed by washing of the extract with water and brine, and then evaporation leaves the crude product, which is purified by flash chromatography on a silica column (eluent, hexane/ethyl acetate = 90/10). Pure α-ketol is analyzed by GC, GC/MS, and ^{13}C and ^1H NMR spectroscopy.

General Procedure for Synthesis of Ketols 3 with $SmCp_2$. In a typical experiment, a solution of 2 mmol of acid chloride dissolved in 10 mL THF is added over a period of 1 h to a suspension of 4.4 mmol $SmCp_2$ in 65 mL THF at −20 °C with use of a syringe pump. At the end of the addition, the reaction mixture is allowed to come to room temperature and then treated as previously.

10-Hydroxy-9-octadecanone: ^1H NMR δ 4.1 (m, 1 H), 3.5 (m, 1 H), 2.4 (dt, J = 7.4 Hz, J' = 1.2 Hz, 2 H), 1.75 (m, 2 H), 1.5 (m, 2 H), 1.4 (m, 2 H), 1.1 (m, 20 H), 0.8 (t, J = 6.1 Hz, 6 H); MS 284 (0.80) M^+, 143 (11.78) $C_8H_{17}CHOH$, 141 (17.86) $C_8H_{17}CO$; IR 3350, 1714, 1400, 1261. Anal. Calcd for $C_{18}H_{36}O_2$; C, 76.00; H, 12.75. Found: C, 75.98; H, 12.75.

5-Hydroxy-2,2,7,7-tetramethyl-4-octanone: ^1H NMR δ 4.08 (d, J = 10.2 Hz, 1 H), 3.42 (m, 1 H), 2.27 (m, 2 H), 1.57 (dd, J = 14.2 Hz, J' = 2.8 Hz, 2 H), 0.98 (s, 18 H); MS 200 (0.86), M^+, 101 (6.0) t-$BuCH_2CHOH$, 99 (8.0) t-$BuCH_2CO$, 71 (5.0) t-$BuCH_2$, 57 (100) t-Bu (obtained as major product in a complex mixture).

1,10-Dichloro-6-hydroxy-5-decanone: ^1H NMR δ 4.1 (m, 1 H), 3.5 (t, J = 6.8 Hz, 4 H), 3.3 (m, 1 H), 2.5 (m, 2 H), 1.7 (m, 10 H); MS 240 (0.74) M^+, 123 (31), 121 (100), 119 (18), $Cl(CH_2)_4CHOH$ and $Cl(CH_2)_4CO$. Anal. Calcd for $C_{10}H_{18}O_2Cl_2$: C, 49.80; H, 7.52; Cl, 29.40. Found: C, 50.23; H, 7.65; Cl, 29.07.

1,2-Dicyclohexyl-2-hydroxyethanone: ^1H NMR δ 4.18 (s, 1 H), 3.40 (m, 1 H), 2.55 (m, 1 H), 1.70 (m, 11 H), 1.18 (m, 10 H); MS 224 (2.50) M^+, 113 (27.24) $C_6H_{11}(CHOH)$, 112 (27.50) $C_6H_{11}CHO$, 111 (10.39) $C_6H_{11}CO$, 83 (65.39) cyclohexyl. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.88; H, 10.79.

1,2-Di(1-adamantyl)-2-hydroxyethanone: ^1H NMR δ 4.04 (s, 1 H), 2.25 (m, 1 H), 1.75 (m, 30 H); ^{13}C NMR δ 218.5, 76.0, 46.8, 38.0, 37.8, 37.4, 36.9, 36.4, 28.1, 27.8; MS 328 (5.0) M^+, 165 (58.8) AdCHOH, 163 (1.7) AdCO, 135 (100) Ad; IR 3480, 1695, 1459, 1378. Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.55; H, 9.59.

General Procedure for Synthesis of Ketols 5 with SmI_2. In a typical experiment, a mixture of 2 mmol of acid chloride and 2 mmol of aldehyde or ketone in 5 mL of THF is rapidly added to a solution of SmI_2 (42 mL; 0.1 N). The reaction mixture turns immediately green and is treated with 0.1 N HCl. Extraction with ether is followed by washing of the extract with water and brine, and then evaporation leaves the crude product, which is purified by flash chromatography on a silica column (eluent, hexane/ethyl acetate = 90/10). Pure α-ketol is analyzed by GC, GC/MS, and ^{13}C and ^1H NMR spectroscopy.

General Procedures for Synthesis of Ketols 5 with $SmCp_2$. In a typical sequential experiment, 4.16 mmol of acid chloride

(31) Iminoacylsamarium species have been recently prepared from isonitriles, organic halides, and SmI_2.[32]

(32) Murakami, M.; Kawano, T.; Ito, Y. *J. Am. Chem. Soc.* **1990**, *112*, 2437.

(33) *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 715.

dissolved in 20 mL of THF is slowly added within 1 h to a well-stirred suspension of $SmCp_2$ (10 mmol) in THF (150 mL) at -20 °C. A brown suspension is obtained. A solution of 4.16 mmol of aldehyde in 5 mL of THF is quickly added. The reaction mixture turns immediately yellow. After 2 h, the solution is treated as previously. Pure α-ketol is analyzed by GC, GC/MS, and ^1H NMR spectroscopy. In another series of experiments (Barbier-type conditions), acid chloride (4.16 mmol) and aldehyde (4.16 mmol) are mixed together in THF (5 mL) and added to a suspension of $SmCp_2$ (10 mmol) in THF (150 mL) at -20 °C.

2,2-Dimethyl-4-hydroxy-3-decanone: ^1H NMR δ 4.5 (m, 1 H), 3.3 (m, 1 H), 1.6 (m, 10 H), 1.20 (s, 9 H), 0.95 (t, J = 7.8 Hz, 3 H); ^{13}C NMR δ 217.9, 72.3, 42.5, 34.8, 31.6, 29.0, 26.7, 25.0, 22.5, 13.9; MS 200 (0.4) M^+, 115 (26.2) $C_6H_{13}CHOH$, 97 (65.7) C_7H_{13}, 85 (6.1) t-BuCO, 57 (100) t-Bu. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.69; H, 11.85.

3,3-Dimethyl-1-hydroxy-1-phenyl-2-butanone: ^1H NMR δ 7.3 (m, 5 H), 5.4 (s, 1 H), 4.4 (m, 1 H), 1.05 (s, 9 H); MS 192 (0.4) M^+, 164 (7.4) M-CO, 107 (100) C_6H_5CHOH, 77 (31) C_6H_5, 57 (51.1) t-Bu. Anal. Calcd for $C_{12}H_{16}O_2$: 74.97; H, 8.38. Found: C, 74.78; H, 8.20.

2,2-Dimethyl-4-hydroxy-3-hexanone: ^1H NMR δ 4.5 (m, 1 H), 3.6 (m, 1 H), 1.6 (m, 2 H), 1.2 (s, 9 H), 0.95 (t, J = 7.9 Hz, 3 H); MS 144 (0.6) M^+, 88 (4.0), 69 (2.7), 57 (100) t-Bu. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.58; H, 11.38.

1-Adamantyl-2-hydroxy-1-butanone: ^1H NMR δ 4.45 (t + s, 1 H), 3.3 (m, 1 H), 1.75 (m, 17 H), 0.9 (t, J = 8.1, Hz, 3 H); MS 222 (3.16) M^+, 193 (0.58) AdCOCHOH, 163 (5.42) AdCO, 135 (100) Ad; IR 3478, 1695, 1452, 1403, 1381. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.50; H, 9.76.

1-Adamantyl-2-hydroxy-2-phenylethanone: ^1H NMR δ 7.35 (m, 5 H), 5.4 (s, 1 H), 4.4 (s, 1 H), 1.6 (m, 15 H); MS 270 (0.3) M^+, 163 (13.1) AdCO, 107 (12.9) PhCHOH, 77 (17.9) Ph. Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15. Found: C, 80.08; H, 8.02.

1-Cyclohexyl-2-hydroxy-1-butanone: ^1H NMR δ 4.31 (m, 1 H), 3.40 (m, 1 H), 2.38 (m, 1 H), 1.6 (m, 12 H), 0.93 (t, J = 8.4 Hz, 3 H); MS 170 (1.50) M^+, 111 (19.5) $C_6H_{11}CO$, 83 (100) cyclohexyl, 59 (35.5) CH_3CH_2CHOH; IR 3320, 1708, 1453, 1417, 1314. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.59; H, 10.81.

2-Hydroxy-1-(1-methylcyclohexyl)-1-butanone: ^1H NMR δ 4.5 (m, 1 H), 1.95 (m, 3 H), 1.5 (m, 10 H), 1.2 (s, 3 H), 1.0 (t, J = 8.8 Hz, 3 H); ^{13}C NMR δ 218.0, 73.4, 46.7, 34.7, 34.1, 28.1, 25.6, 23.7, 22.5, 22.3, 9.3; MS 184 (0.36) M^+, 125 (3.60) M - C_3H_7O, 97 (100) methylcyclohexyl, 88 (11.14) $CH_3CH_2CH(OH)CHO$; IR 3478, 1698, 1457, 1403, 1378. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.59; H, 10.95.

2-Hydroxy-1-(1-methylcyclohexyl)-2-phenylethanone: ^1H NMR δ 7.35 (m, 5 H), 5.45 (m, 1 H), 4.45 (m, 1 H), 1.4 (m, 10 H), 0.9 (s, 3 H); MS 215 (0.2), 136 (2.6) PhCH(OH)CHO, 125 (13.1) $CH_3C_6H_{10}CO$, 107 (33.4) PhCHOH, 97 (100) methylcyclohexyl, 77 (22.3) Ph. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.43; H, 8.39.

3-Hydroxy-4-dodecanone: ^1H NMR δ 4.4 (m, 1 H), 4.2 (m, 1 H), 2.5 (m, 2 H), 1.7 (m, 2 H), 1.3 (m, 12 H), 0.95 (m, 6 H); MS 200 (0.89) M^+, 141 (28.98) $C_8H_{17}CO$, 59 (100) CH_3CH_2CHOH; IR 3492, 1715, 1461, 1411. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.07. Found: C, 72.16; H, 11.89.

1-(1-Hydroxycyclohexyl)-1-nonanone: ^1H NMR δ 3.6 (m, 1 H), 2.55 (t, J = 8.1 Hz, 2 H), 1.67 (m, 10 H), 1.27 (m, 12 H), 0.88 (t, J = 6.2 Hz, 3 H); ^{13}C NMR δ 214.2, 77.2, 35.0, 33.1, 31.1, 28.7, 28.6, 28.4, 24.6, 23.1, 21.9, 20.4, 13.4; MS 241 (0.63) M^+, 141 (0.45) $C_8H_{17}CO$, 99 (100) $C_6H_{10}OH$, 81 (30.79) cyclohexenyl. Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.01; H, 11.48.

1-(1-Hydroxycyclohexyl)ethanone: ^1H NMR δ 3.6 (m, 1 H), 2.25 (s, 3 H), 1.6 (m, 10 H); MS 143 (0.16) M^+, 99 (98) $C_6H_{10}OH$, 81 (100) cyclohexenyl. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.33; H, 9.96.

Note Added in Proof: We recently found that benzoyl chloride gives **3** mainly when quenching is performed in anaerobic conditions. Benzil **2** has been therefore produced by very fast air oxidation of precursor ene diol prior to tautomerization to **3** (for a similar observation, see: Duhamel, L.; et al. *Tetrahedron Lett.* **1983**, *24*, 4209).

Binding of Dihydroxybenzenes in Synthetic Molecular Clefts

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Received June 22, 1990

Synthetic molecular clefts of type 1 strongly bind dihydroxybenzenes in organic solvents. The association constants have values up to 3×10^5 M^{-1}. The guests are sandwiched between the *o*-xylylene walls of the host and form hydrogen bonds with the receptor.

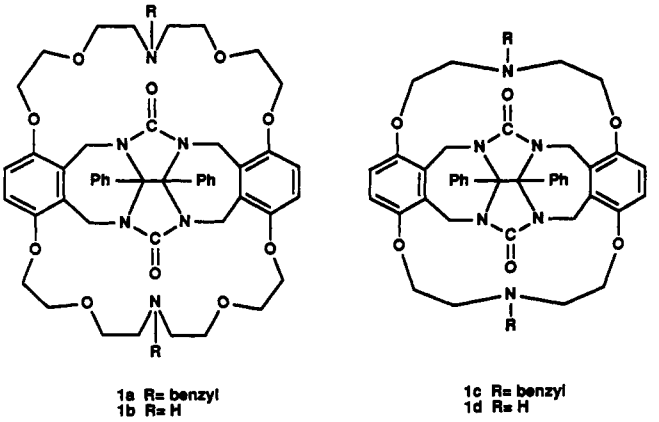
Introduction

In the growing field of host–guest chemistry, much work is currently being directed toward the development of receptors that recognize neutral molecules in aqueous as well as in organic solvents.[1] Recognition is an important step in enzymatic catalysis, in selective transport, and in various other biological processes in living systems. Research on host–guest systems has mostly been focused on two aspects: (i) to gain a better understanding of the intermolecular interactions involved and (ii) to attain the same high selectivity as found in the natural systems.

We are interested in selective synthetic receptors for dihydroxybenzenes (DHB's) as part of our program aimed at the development of a dopamine β-hydroxylase mimic.[2]

In this paper we report on the strong complexation of DHB's in the new synthetic receptors **1a–d**[3] (Chart I).

Chart I



These compounds contain a cleft which is formed by a diphenylglycoluril unit and two *o*-xylylene rings. These

(1) Diederich, F. *Angew. Chem.* **1988**, *100*, 372.
(2) Martens, C. F.; Nolte, R. J. M. To be published.

0022-3263/91/1956-3122$02.50/0