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Preliminary communication

$Et_3GeNa–YCl_3$ complex as a new strong base

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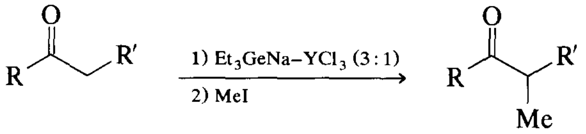
Abstract

The complex $Et_3GeNa–YCl_3$ (3 : 1) as a new strong base reacted with a variety of ketones to yield the corresponding enolate anions in good yields.

Keywords: Germanium; Yttrium; Germyl anion; Base

Group-14-element–alkali-metal species as nucleophiles have been extensively studied in organic and organometallic syntheses, e.g. the introduction of Group 14 elements into organic halides, metal halides, carbonyl compounds, etc. [1–3] However, few reports have described the generation of metal enolates by use of these Group 14 element-centered anions as bases [4,5]. In the course of our studies on organogermanium–alkali metal species [3], we observed that $Et_3GeNa–YCl_3$ (3 : 1) was a strong base which is useful for abstraction of a proton from the carbon atom of a carbonyl group. We report herein the first selective methylation of various ketones by treatment with $Et_3GeNa–YCl_3$ (3 : 1) and methyl iodide (MeI) as shown in Scheme 1.

The results of methylation of ketones by Et_3GeM (M = Li, Na, K or Rb) and MeI under various conditions are summarized in Table 1. As shown, the products formed by the reaction of Et_3GeM and MeI with acetophenone depended on the alkali metal, additives, and solvents used. Et_3GeM only promoted the reaction of acetophenone with MeI to give propiophenone together with isobutyrophenone (and α-germylcarbinols) under certain reaction conditions (Table 1, Entries 1, 9, 10, 11). Among alkali-metal–additive–solvent combinations, M = $Na–YCl_3$–HMPA/THF was most successful for monomethylation of acetophenone (Table 1, entry 4). The yield of propiophenone increased with decreasing concentration of YCl_3 and reached a maximum when the ratio of Et_3GeNa and YCl_3 was 3 : 1 [6]. In less polar solvents such as toluene and hexane, the desired ketone was obtained only in low yields (Table 1, entries 5, 6). Other lanthanoid metal salts (scandium(III) chloride, samarium(III) chloride, yttrium(III) chloride) were less effective than that germanium counterparts (Table 1, entries 2, 7, 8). The complex $Et_3GeNa–YCl_3$ in HMPA/THF also reacted with other aryl ketones, cyclic ketones and alkyl ketones to yield the corresponding monomethylated products in good yield (97–98%) (Entries 12–15). No reaction took place when Et_3GeNa was absent [7].



Scheme 1.

2-Methylcyclohexanone affords the corresponding 6-methylated products (2,6-dimethylcyclohexanone : 2,2-dimethylcyclohexanone, 99 : 1) selectively (Scheme 2).

To obtain information on the $Et_3GeNa–YCl_3$ complex base, NMR studies were carried out. A small downfield shift of the ^1H NMR signals for the complex with a slight upfield shift of the ^{13}C NMR ones [8], as compared with those of Et_3GeNa [9], suggests the formation of $(Et_3Ge)_3Y$.

According to the present results, it is clear that $Et_3GeNa–YCl_3$ can be employed as a kinetically selective base, like lithium diisopropylamide (LDA), lithium

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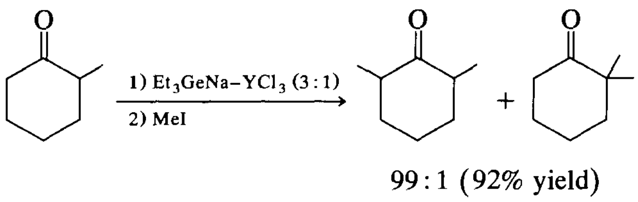

Scheme 2.

isopropylcyclohexylamide (LICA), potassium hexamethyldisilylamide (KHDS), etc. [10]. In particular, $Et_3GeNa–YCl_3$ easily prepared by $Et_3GeGeEt_3$, Na and YCl_3, is an efficient base for the preparation of enolate anions of alkyl ketones.

A typical experimental procedure is described below for the reaction of acetophenone with $Et_3GeNa–YCl_3$ and MeI. To a YCl_3 (0.38 mmol) suspension in THF (1 ml) was added Et_3GeNa prepared from the reaction of $Et_3GeGeEt_3$ (0.57 mmol) and sodium metal (4.2 mmol) in a mixture of THF (5 ml) and HMPA (2.5 ml) [11] by means of a syringe, and the mixture was stirred for 2 h at room temperature. Acetophenone (1 mmol) was added and the mixture stirred for a further 1 h. After cooling to −78°C, MeI (1.2 mmol) was introduced and the mixture was stirred for 1.5 h. The reaction mixture was passed through a short column of silica gel and eluted with ether. After the usual work-up, propiophenone was obtained in a 98% yield.

In summary, we have developed a useful strong base $Et_3GeNa–YCl_3$ (3 : 1). This complex promoted the reaction of various ketones with MeI to give the corresponding monomethylated products in good yield. Further investigations into the synthetic applications of this complex and the identification of the intermediate active species are now in progress.

Acknowledgments

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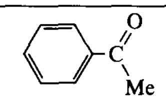
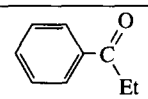
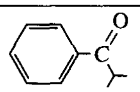
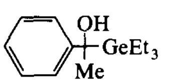
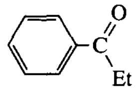
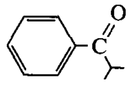
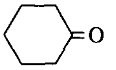
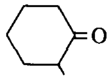
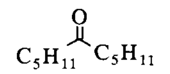
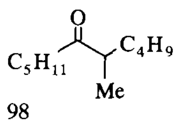
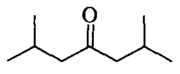
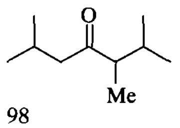
Table 1
Methylation of metal enolates generated from ketones and Et_3GeM under various conditions [a]

Entry	Et_3GeM	Ketone	Additive	Solvent	Products and Yields (%) [b]		
1	Na		none	HMPA-Et_2O	 45	 27	 0
2	Na	as 1	$ScCl_3$	HMPA-Et_2O	18	27	8
3	Na	as 1	YCl_3	HMPA-Et_2O	85	27	0
4	Na	as 1	YCl_3	HMPA-THF	98	trace	0
5	Na	as 1	YCl_3	HMPA-toluene	54	21	3
6	Na	as 1	YCl_3	HMPA-hexane	36	7	7
7	Na	as 1	$SmCl_3$	HMPA-Et_2O	21	17	9
8	Na	as 1	$YbCl_3$	HMPA-Et_2O	19	35	43
9	Li	as 1	none	HMPA-Et_2O	6	0	53
10	K	as 1	none	HMPA-Et_2O	11	26	0
11	Rb	as 1	none	HMPA-Et_2O	14	9	0
12	Na		YCl_3	HMPA-THF	 98		
13	Na		YCl_3	HMPA-THF	 97		
14	Na		YCl_3	HMPA-THF	 98		
15	Na		YCl_3	HMPA-THF	 98		

[a] Reactions of Et_3GeM (1.0 equiv.)–additive (0.33 equiv.) with ketones (1.0 equiv.) and MeI (1.2 equiv.) were carried out at at −78°C.
[b] Isolated yields.

References and notes

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[2] For examples see (a) D.A. Armitage, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds), *Comprehensive Organometallic Chemistry*, Vol. 2, Ch. 9, Pergamon, New York, 1982, pp. 99–104; (b) H. Sakurai, *Kagaku no Ryoiki, 30* (1976) 67; (c) M. Fujita and T. Hiyama, *Yukigosei Kagaku Kyokaishi, 42* (1984) 293.

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[6] Propiophenone was obtained in 68% and 24% yields when YCl_3 (0.5 and 1.0 equiv., respectively) was used.

[7] When $PhMe_2GeNa$ or Hex_3GeNa was used instead of Et_3GeNa, the desired product was obtained in low yield (38%).

[8] ^1H NMR (δ in HMPA–THF-d_8) of $Et_3GeNa–YCl_3$ (3:1) 0.16 (q), 0.93 (t). ^{13}C NMR 17.33 (C_1), 15.36 (C_2). In the ^1H NMR spectrum two small triplet signals (0.77 and 0.83 ppm) were also observed.

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