Alkylidenation of Ketones by *gem*-Dibromoalkane, SmI_2, and Sm in the Presence of Catalytic Amount of $CrCl_3$

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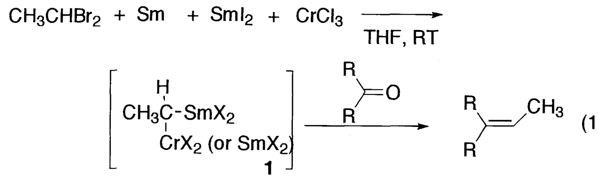
Alkylidenation of ketones can be performed by the reaction with geminal dibromoalkane-SmI_2-Sm in the presence of catalytic amount of $CrCl_3$ at room temperature yielding the alkylidenated products in good to excellent yields.

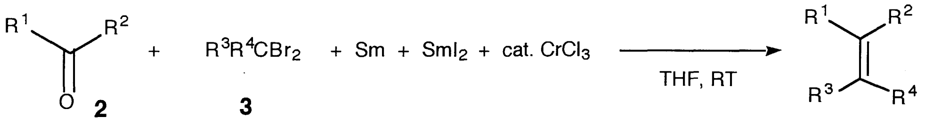
Wittig reaction has opened novel synthesis of olefins in a selective fashion.[1] Although the reaction is one of the most promising for the chemo- and stereoselective alkylidenation of carbonyl groups, limitation of the applications has been disclosed. Recently developed reaction of carbonyl groups with *gem*-dimetallic species has played compensatory roles in olefin syntheses.[2] Chemoselectivity of the reaction with *gem*-dimetallic species strongly depends upon the properties of the metal; aldehyde-selective olefination can be performed by *gem*-dichromium reagents[3a] and ester-carbonyl olefination is realized by the use of Ti-Zn system.[3b-d] Dimetallic reagents using lanthanoid as the key element are expected to possess high nucleophilicity and low basicity;[4-6] the reagents are expected to apply the olefination of easily enolizable ketones. This paper describes the generation of *gem*-dimetallic reagents by the reduction of *gem*-dihaloalkanes with low valent metal systems Sm-SmI_2 under $CrCl_3$ catalysis. The reagent can be successfully applied to the olefination of easily enolizable ketones (eq 1).



(1)

Typical procedure is as follows. To a mixture of Sm powder (20-40 mesh, 0.30 g, 2.0 mmol), SmI_2 (0.1 M in THF, 20 ml, 2.0 mmol), and anhydrous $CrCl_3$ (0.16 g, 0.1 mmol), was added

Table 1. Alkylidenation of ketones with $RCHBr_2$, Sm, SmI_2, and $CrCl_3$ [a]



Entry	Ketone **2** (1.0 mmol)	$R^3R^4CBr_2$ **3** (2 mmol)	Reagent (mmol) SmI_2	Sm	$CrCl_3$	**4** Yield (%)[b] (E/Z)
1	4-t-Butylcyclohexanone	CH_3CHBr_2	8	0	0	not detected[c]
2			2	2	0	22[c]
3			8	0	0.1	37
4			2	2	0.1	71
5		CH_3CHI_2	2	2	0.1	29
6		$CH_3(CH)_4CHBr_2$	2	2	0.1	65
7	2-Undecanone	CH_3CHBr_2	2	2	0.1	67 (50 / 50)
8	Cyclopentanone	$CH_3(CH)_4CHBr_2$	2	2	0.1	51
9	β-Tetralone		2	2	0.1	71 (56 / 44) [d,e]
10	t-Butyl methyl ketone	$CH_3(CH_2)_4CHBr_2$	2	2	0.1	71 (64 / 36) [d,e]
11	Diisopropyl ketone		2	2	0.1	61 [e]
12	4-t-Butylcyclohexanone	$(CH_3)_2CBr_2$	2	2	0.1	53
13		$EtOCOCHBr_2$	2	2	0.1	38
14		$Me_3SiCHBr_2$	2	2	0.1	54
15		$Me_3SnCHBr_2$	2	2	0.1	40 [f]
16	Trimethylsilyl heptyl ketone	CH_3CHBr_2	2	2	0.1	54 (66 / 34)
17		$Me_3SiCHBr_2$	2	2	0.1	56 (80 / 20)

[a] Sm powder (20 – 40 mesh), SmI_2 (0.1 M in THF), and anhydrous $CrCl_3$ were used. [b] Isolated yields. [c] 4-t-Butyl-1-iodoethyl-cyclohexanol was detected: 18% yield (entry 1) and 8% yield (entry 2). [d] The E/Z configuration was not assigned. [e] A treatment of the ketones with triphenylethylidenephosphorane did not give any ethylidenated product and resulted in the recovery of the ketones: >95% (entry 9), 80% (entry 10), and 72% (entry 11). [f] 4-t-butyl-1-methylidenecyclohexane was also obtained in 19% yield.

a mixture of 1,1-dibromoethane (0.38 g, 2.0 mmol) and 4-t-butylcyclohexanone (0.15 g, 1.0 mmol) in THF (2 ml) at room temperature. The mixture was stirred for 0.5 h at the same temperature. The resulting mixture was diluted with hexane (50 ml) and filtered through a short silica gel column. The filtrate was concentrated. A further purification by a silica gel column chromatography gave 4-t-butyl-1-ethylidenecyclohexane in 71% yield (0.12 g). Other results are summarized in Table 1.

For the efficient alkylidenation, both low valent samarium and chromium salt were indispensable. A treatment of a mixture of 4-t-butylcyclohexanone and 1,1-dibromohexane with the stoichiometric amount of chromium(II) chloride ($CrCl_2$) resulted in a quantitative recovery of starting materials.[7] A combination of SmI_2 and Sm worked more effectively compared to the use of SmI_2 alone (entries 2,4).[8] A treatment of *gem*-dibromoalkane with SmI_2 and Sm in the presence of $CrCl_3$ gave the best yield, while a use of geminal diiodide resulted in the poor yield of the alkene (entry 5). As the characteristic point of the alkylidenation reagent, a strong nucleophilicity was representative. Easily enolizable ketones such as cyclopentanone and β-tetralone were converted into the corresponding alkenes (entries 8,9). The alkylidenations of sterically hindered ketones such as t-butyl methyl ketone and diisopropyl ketone proceeded in good yields (entries 10,11). Uses of dibromomethyltrimethylsilane and dibromomethyltrimethylstannane lead to the preparations both alkenylsilanes[3d] and alkenylstannanes[9] from ketones (entries 14,15,17).

Any direct evidence of the dimetallic species has not been obtained, but the following results imply the existence of these species. While a treatment of 1,1-dibromoundecane (1.0 mmol) with Sm (1.0 mmol) and SmI_2 (1.0 mmol) afforded 1-undecene in 84% yield after aqueous work-up (eq 2), a similar treatment in the presence of $CrCl_3$ (0.1 mmol) gave a mixture of 1-undecene and undecane (54 / 46) in 70% yield after aqueous work-up (eq 3).[10-12] The alkane should be yielded after a protonation of the dimetallic species.[13]

$$\text{n-}C_{10}H_{23}CHBr_2 + Sm + SmI_2 \longrightarrow \underset{84\%}{\text{n-}C_9H_{19}CH{=}CH_2} \qquad (2)$$

$$\text{n-}C_{10}H_{23}CHBr_2 + Sm + SmI_2 + \text{cat. } CrCl_3 \longrightarrow \underset{70\%\ (54:46)}{\text{n-}C_9H_{19}CH{=}CH_2 + \text{n-}C_{11}H_{24}} \qquad (3)$$

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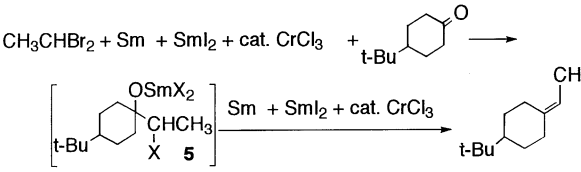
10 Although we are assuming *gem*-dimetallic species as the reactive species in these alkylidenation reactions (eq 1), a stepwise mechanism was also proposed as an alternative route to the alkene (eq 4).[11] The stepwise mechanism, however, is unlikely in our case, as the reduction and elimination step (**5** → alkene) was relatively slow under the reaction conditions. Compound **5** (X=I) was prepared by a treatment of 4-t-butylcyclohexanone and 1,1-diiodoethane with SmI_2 in 92% yield.[5] Even use of 1,1-dibromoethane gave iodo-hydrine **5** (X=I). The obtained THF solution of **5** (2.0 mmol) was treated with Sm (1.5 mmol), SmI_2 (1.5 mmol) and $CrCl_3$ (0.2 mmol) at 25 °C. 4-t-Butyl-1-ethylidene-cyclohexane was obtained in 11% yield and 4-t-butyl-1-iodoethylcyclohexanol was obtained in 1.2% yield after 5 min; in 43% yield and in 11% yield after 0.5 h. On the contrary, a treatment of 4-t-butylcyclohexanone with Sm, SmI_2, and $CrCl_3$ catalyst as shown in eq 1 yielded the alkene in 61% within 5 min; in 71% after 0.5 h.



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12 A work-up with DCl in D_2O did not give any deuterated product. A difficulty of deuteration of organosamarium species was also mentioned in H. B. Kagan, J. Collin, J. L. Namy, C. Bied, F. Dallemer, and A. Lebrun, *J. Alloys Comp.*, **192**, 191 (1993).

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