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Siloxycarbenium Tetrakis[3,5-bis(trifluoromethyl)phenyl]borates and Their Role in Reactions of Ketones with Nucleophiles[1)]

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The intermediacy of trialkylsiloxycarbenium ions was demonstrated by NMR spectroscopy during the reduction of ketones with hydrosilanes catalyzed by trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. It is suggested that the non-nucleophilic nature of the counter anion plays an important part in the modification of the reaction courses.

Trialkylsilyl-based Lewis acids (R_3Si-X; X = triflate,2,3) iodide,3) and perchlorate4)) have been utilized as catalysts for the reactions of carbonyl compounds with various nucleophiles such as hydrosilanes and allylsilanes. Although siloxycarbenium ions have often been assumed as key intermediates in these reactions, no direct spectroscopic evidence for the existence in solution has been reported until now.. We have found by means of NMR spectroscopy that the siloxycarbenium ions are produced as stable chemical species at low temperatures in dichloromethane during the reaction of hydrosilanes with trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) as well as the reaction of NaTFPB5) with chlorosilanes in the presence of ketones. The remarkable modal shift for the reduction of ketones has been demonstrated by using formal trialkylsilyl TFPB as a Lewis acid catalyst.

Typically, when trimethylchlorosilane was mixed with NaTFPB in CD_2Cl_2 in the presence of benzophenone (the molar ratio of Me_3SiCl/NaTFPB/benzophenone = 2:1:2) at -20 °C, the major formation of trimethylsiloxydiphenylcarbenium ion (**1a**) was observed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Method A). The structure of **1a** was characterized on the basis of the significantly low ^{29}Si resonance at 52.3 ppm in comparison with that for Me_3SiCl (33.0 ppm), and of the ^{13}C resonance for carbenium carbon at 208.3 ppm, which was in good agreement with the corresponding value for diphenyl(hydroxy)carbenium ion (209.5 ppm);6) the ^{1}H and ^{13}C resonances for trimethylsilyl moiety in **1a** appeared at 0.54 and 0.4 ppm, respectively. The yield of **1a** was determined by ^{1}H NMR to be 91% based on the consumed trimethylchlorosilane. The signals assigned to **1a** did not change at -20 °C for more than 1 day.

The formation of siloxycarbenium ion **1a** was also observed during the NMR investigation of the reaction of trimethylsilane in the presence of benzophenone with trityl TFPB, which was pregenerated as a yellow solution by mixing triphenylchloromethane with an equimolar amount of NaTFPB in CD_2Cl_2 (Method B). Thus, the reaction among Me_3SiH/trityl TFPB/Ph_2CO (>10:1:2) at -30 °C gave **1a** in ca. 60% yield based on the starting trityl TFPB, together with significant amounts of trimethylfluorosilane, hexamethyldisiloxane, and diphenylmethane.

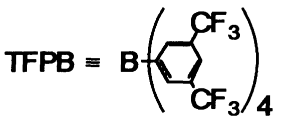
Method A

$$\mathrm{Me_3SiCl} + \mathrm{NaTFPB} \xrightarrow[\mathrm{CD_2Cl_2}]{\mathrm{Ph_2C{=}O}} \underset{\mathbf{1a}}{[\mathrm{Ph_2C{=}\overset{+}{O}{-}SiMe_3}]\mathrm{TFPB^-}} + \mathrm{NaCl} \tag{1}$$

Method B

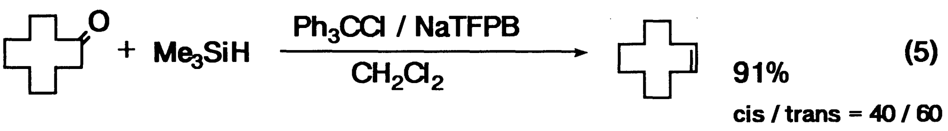
$$\mathrm{Ph_3CCl} + \mathrm{NaTFPB} \xrightarrow{\mathrm{CD_2Cl_2}} \mathrm{Ph_3C^+\,TFPB^-} + \mathrm{NaCl} \tag{2}$$

$$\mathrm{Me_3SiH} + \mathrm{Ph_3C^+\,TFPB^-} \xrightarrow[\mathrm{CD_2Cl_2}]{\mathrm{Ph_2C{=}O}} \mathbf{1a} + \mathrm{Ph_3CH} \tag{3}$$



In order to explore the role of trialkylsiloxycarbenium ions having TFPB as a counter anion in the reactions of ketones with trialkylsilanes catalyzed by trityl TFPB, we have investigated the following reactions on a preparative scale. Thus, to a yellow solution of a mixture of benzophenone (186 mg, 1.02 mmol), triphenylchloromethane (27 mg, 0.10 mmol) and NaTFPB (84 mg, 0.09 mmol) in dichloromethane (5 ml), was added triethylsilane (433 mg, 3.72 mmol). After stirring for 2 h at room temperature, column chromatography (silica-gel, hexane) followed by the preparative TLC (hexane) gave diphenylmethane (150 mg, 0.89 mmol) in the yield of 87%. Reduction of cyclododecanone with excess trimethylsilane under a similar reaction condition gave cyclododecene in 91% yield (the cis/trans ratio, 40/60).(7) A similar reduction of adamantanone gave a mixture of adamantane, 2-adamantanol, and di-adamantyl ether, whose yields significantly depended on the reaction conditions; the yields were 8, 15, and 75%, respectively, when $\mathrm{Me_3SiH}$ was introduced to a mixture of adamantanone and catalytic amounts of $\mathrm{Ph_3CCl}$ and NaTFPB (1:1) in $\mathrm{CH_2Cl_2}$, while the yields were 26, 40, and 29%, respectively, when a catalytic amount of $\mathrm{Me_3SiCl}$ was added to a mixture of adamantanone, a large excess of $\mathrm{Me_3SiH}$, and a catalytic amount of NaTFPB.

$$\mathrm{Ph_2CO} + \mathrm{Et_3SiH} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Ph_3CCl\ /\ NaTFPB}} \underset{87\%}{\mathrm{Ph_2CH_2}} \tag{4}$$



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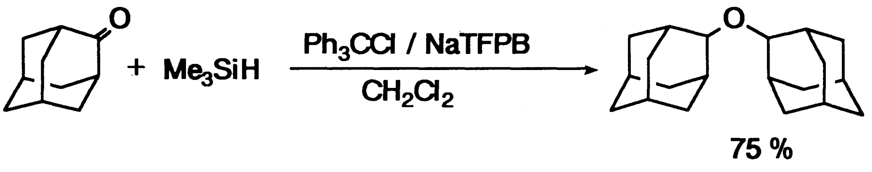
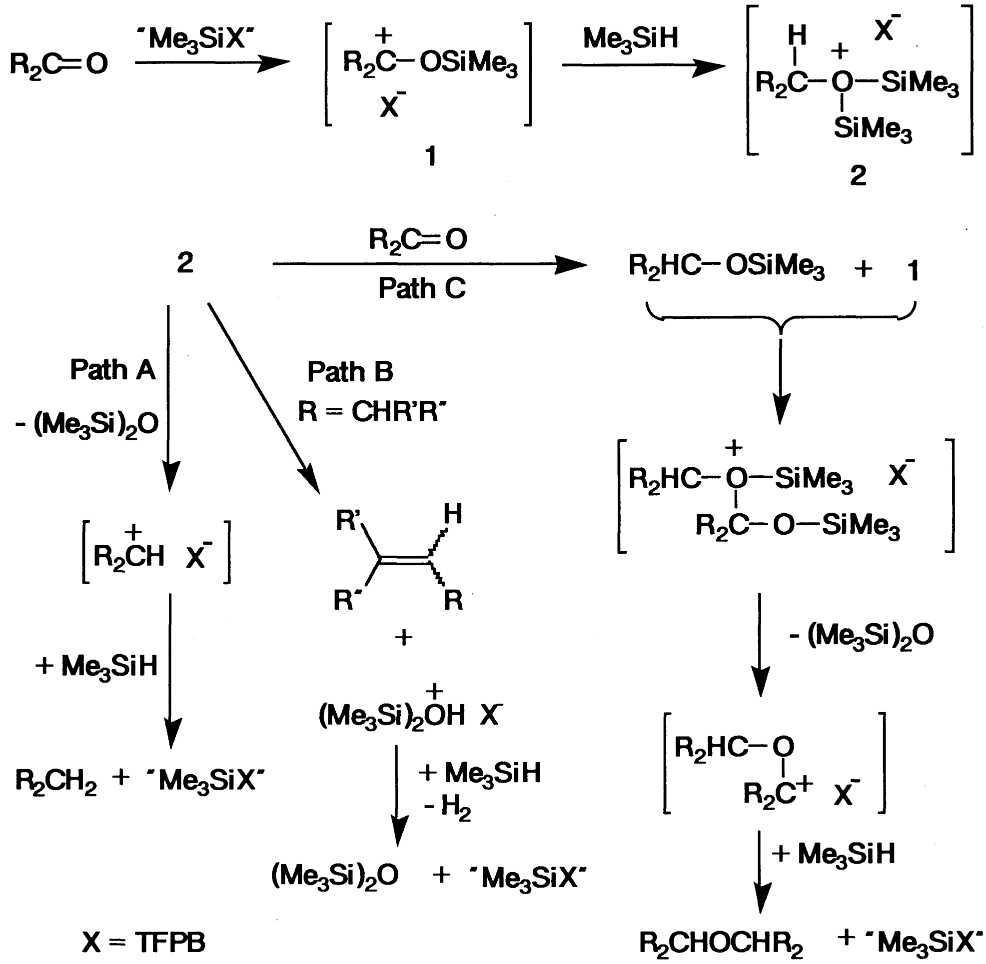


(6)

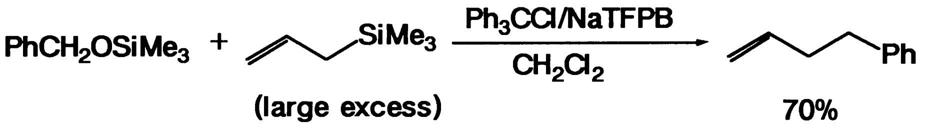
The siloxycarbenium ions (**1**) will be a common intermediate in these reactions as shown in Scheme 1. Thus, **1** which is formed by the reaction of trityl TFPB with trialkylsilane in the presence of a ketone, abstracts hydride from trialkylsilane giving bis(trialkylsilyl)oxonium ion **2**. When R = Ph, **2** eliminates hexamethyldisiloxane giving diphenylmethyl cation (**3a**), which in turn abstracts hydride from trialkylsilane to yield diphenylmethane (Path A). The β-elimination takes place preferably from the bis(trialkylsiloxy)-oxonium ion **2b** which is produced from cyclododecanone, giving cyclododecene (Path B). Finally, since the β-elimination is prevented in the case of **2c** prepared from adamantanone, the third pathway giving siloxyadamantane and diadamantyl ether (Path C) competes with Path A. Path C will be followed by a similar pathway proposed by Olah et al.[3] for the reaction of aliphatic ketones with trialkylsilanes in the presence of R_3SiOTf and R_3SiI, giving the corresponding dialkyl ethers in good yields.

Non-nucleophilic nature of the TFPB anion would be crucial for the formation of bis(trialkylsilyl)-oxonium ions **2** as an important intermediate; trialkylsilyl TFPB is a rather imaginary existense, and therefore, even if it is formed, it will immediately add to a silyl ether giving **2**.[8] On the other hand, **2** would not intervene during the reactions when covalent silyl-based Lewis acids such as R_3SiOTf or R_3SiI are used as a catalyst.



Scheme 1.

As suggested by the intermediacy of 2 in the reduction of ketones with hydrosilanes, an allyl coupling between benzyl trimethylsilyl ether and allyltrimethylsilane ocurred in the presence of a catalytic amount of trityl TFPB. Thus, the allylation of benzyl trimethylsilyl ether with ten equivalents of allyltrimethylsilane gave 4-phenyl-1-butene in the isolated yield of 70%, whereas the yield was lowered to be 10% when an equivalent of allyltrimethysilane was used. Benzyl TFPB formed from benzylbis(trimethylsilyl)oxonium ion would add to allyltrimethylsilane giving 4-phenyl-1-butene, while the competitive addition of the benzyl cation to aromatic rings gives the undesired side products. In this context, it is noteworthy that the reaction of benzyl methyl ether does not react with allyltrimethylsilane in the presence of $TiCl_4$, while it activates the allyl coupling between benzyl halides and allyltrimethylsilane.[9)]



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