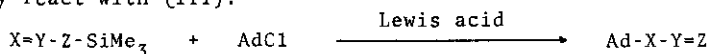


SYNTHESIS OF ADAMANTANE-HETEROCYCLES BY THE ELECTROPHILIC
SUBSTITUTION REACTION WITH UNSATURATED SILANES

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The synthetic study of adamantane derivative is of considerable interest in both mechanistic and pharmacological viewpoints, and numerous preparative methods have been developed. In the substitution reactions at the adamantane bridgehead, nucleophilic conditions are disfavored and they have been realized mostly under electrophilic conditions. In the past decade, organosilicon compound has been shown to have wide applicability in organic synthesis. Lack of its reactivity sometimes gives advantages over other metals under the appropriate conditions. Substitution at the adamantane bridgehead is the case; we have revealed that allylsilane and its heteroanalogues successfully react with (III).



For example, $\text{CH}_3\text{CON}(\text{Me})\text{-SiMe}_3$ as a typical case of X=N , Y=C , Z=O , was treated with (III) in CHCl_3 in the presence of 2 eq. of AlCl_3 at room temperature to give N-adamantyl acetamide. By applying this procedure to the ring system containing X=Y-Z-SiMe_3 moiety it was possible to obtain adamantane-heterocycles. First studied are simple five-membered rings: Trimethylsilylated 2-pyrrolidone, succinimide, and 2-imidazolidinone reacted with (III) under the above conditions to give N-adamantyl derivatives respectively. Reaction of 3-methylisoxazolin-5-one gave also N-adamantylated product. Unsuccessful substitution on N-trimethylsilylpyrrolidine indicates that $-\overset{\text{O}}{\text{C}}\text{-N-}$ unit is required to perform the substitution on nitrogen. Uracil and pyridone are also entried as a reactive heterocycles with (III). Likewise catalytic reaction could introduce adamantyl group on these rings. However steric hindrance caused no reaction when a substituent exists at the neighbour of reactive nitrogen. Thioanalogue (X=S , Y=C , Z=N) reacted also with (III), but S-adamantylation was observed in this case.

Electrophilic substitution reaction toward some silylated heteroaromatics (ex. silyl-imidazole and triazole) were attempted. Interestingly adamantylation occurred at a position distinct from that of acylation, indicating adamantylation was not influenced by the directing effect of silyl group. Furthermore Friedel-Crafts acylation was achieved by using 2-trimethylsilylfuran and -thiophene with (IV) under the Lewis acid catalyzed conditions.