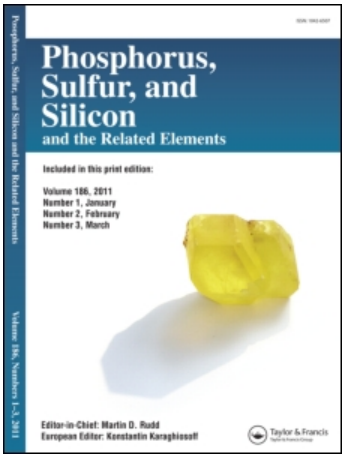

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Ambident Cationic Behavior of [SCN+]: Reactions of Vinyl and Allyl Metals with TMSNCS/ Halogen-Oxidants Agent

YOO TANABE, KEI MORI, and NORISADA KAWABATA
School of Science, Kwansei Gakuin University, 1-1-155 Uegahara, Nishinomiya, Hyogo 662, Japan

The first and clear ambident character of the SCN cation during the reaction with vinylic and allylic metals are described.

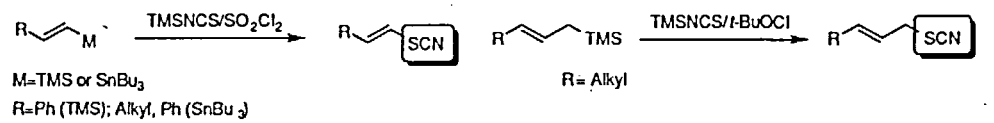
INTRODUCTION

Thiocyanato anion [SCN^-] is known as a representative "ambident anion". On the other hand, all the electrophilic reactions of the thiocyanato cationic species [SCN^+], which are generated from $(SCN)_2$ or ClSCN, exclusively produce thiocyanates (R-SCN).

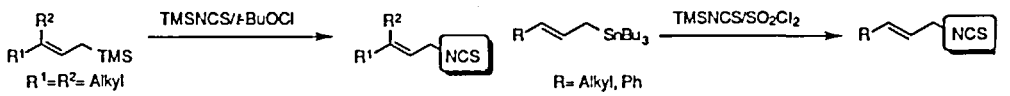
RESULTS AND DISCUSSION

We describe here (TMSNCS)/halogen oxidizing agents working as an "ambident cation" toward vinyl and allyl metals (silanes and tins). To the best of our knowledge, this is the first phenomena of ambident cationic species [SCN^+] in organic reactions.

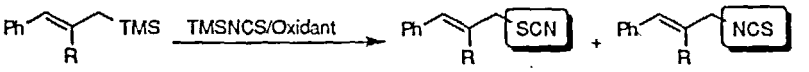
(1) Highly selective formation of R-SCN:



(2) Highly selective formation of R-NCS:



(3) Borderline case:



	N-Cl-Succinimide	$PyHBr_3$
R=H	0:100	5.6:1
R=Me	1:18	3.5:1

Based on these results, we propose the relationship between the reactivity c substrates and the selectivity as shown in the following scheme.