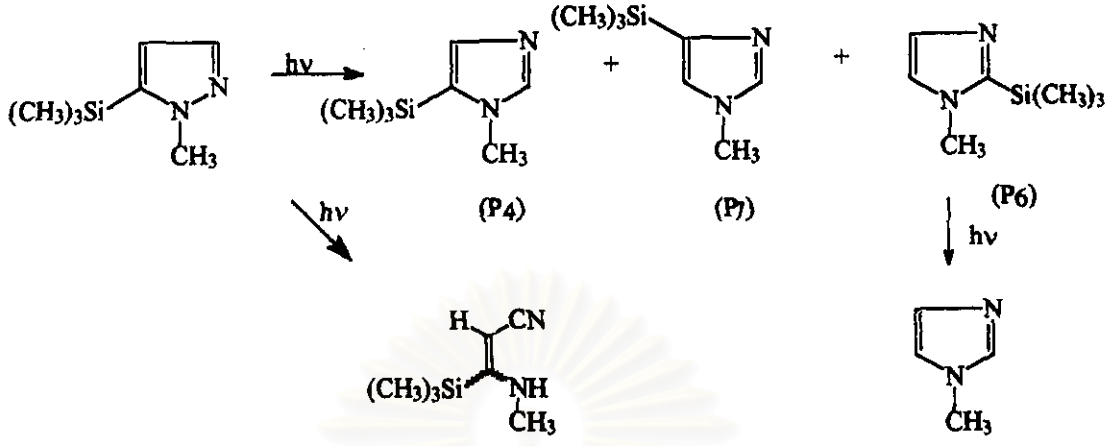
CHAPTER IV

CONCLUSION

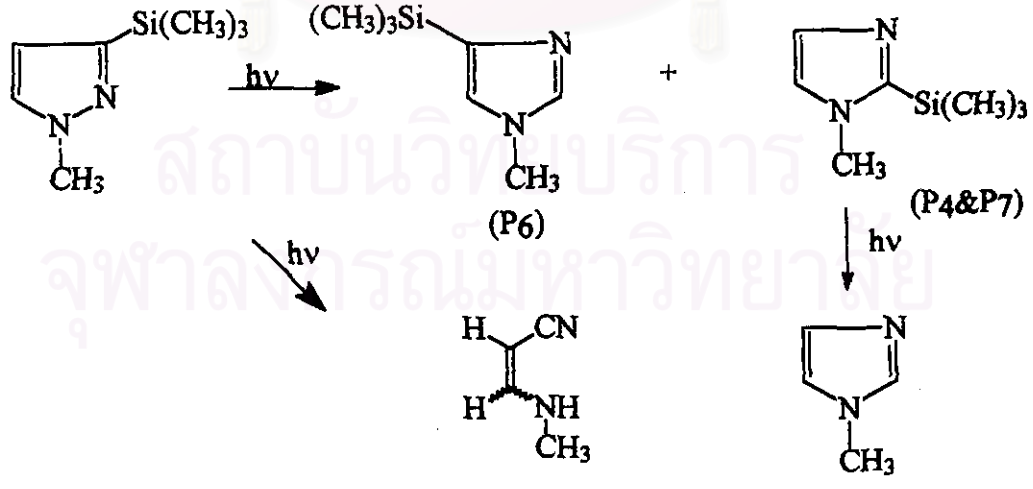
4.1 Photoreactions of 5-(trimethylsilyl)-1-methylpyrazole and 3-(trimethylsilyl)-1-methylpyrazole

Photoisomerization reactions of 3- and 5-(trimethylsilyl)-1-methylpyrazole have been investigated. The study dealt with determining the identity of the photoproducts formed. All main products have been identified and for most, by application of the permutation process approach. The permutation patterns consistent with the phototransposition reaction have been established.

5-(Trimethylsilyl)-1-methylpyrazole underwent phototransposition to three photoproducts as welll as photocleavage to the other product. The phototransposition products were 5-(trimethylsilyl)-1-methylimidazole as a major product of P_4 process, 4-(trimethylsilyl)-1-methylimidazole as a predicted product of P_7 process, and 1-methylimidazole. The last product was assumed to be the secondary product arising from 2-(trimethylsilyl)-1-methylimidazole which is a P_6 photoproduct. This is due to unstability of trimethylsilyl substituent to moisture and particularly the irradiation. The photocleavage product was identified as cis and trans isomers of 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitriles.

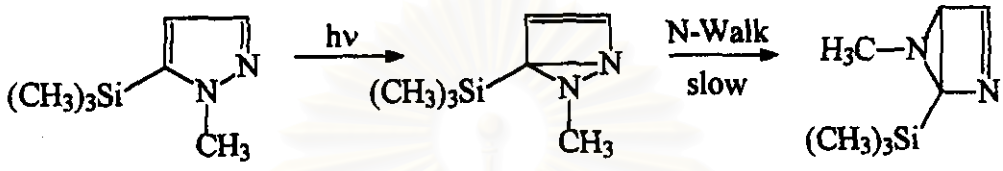


3-(Trimethylsilyl)-1-methylpyrazole underwent phototransposition to two photoproducts as well as photocleavage to one product. The phototransposition product were 4-(trimethylsilyl)-1-methylimidazole, as a predicted product of P_6 process and 1-methylimidazole which was the *secondary* product arising from 2-(trimethylsilyl)-1-methylimidazole, as a product of P_4 & P_7 processes, losing trimethylsilyl group during the irradiation. The photocleavage product was identified to be *cis trans* isomers of 3-(*N*-methylamino)propenenitriles.

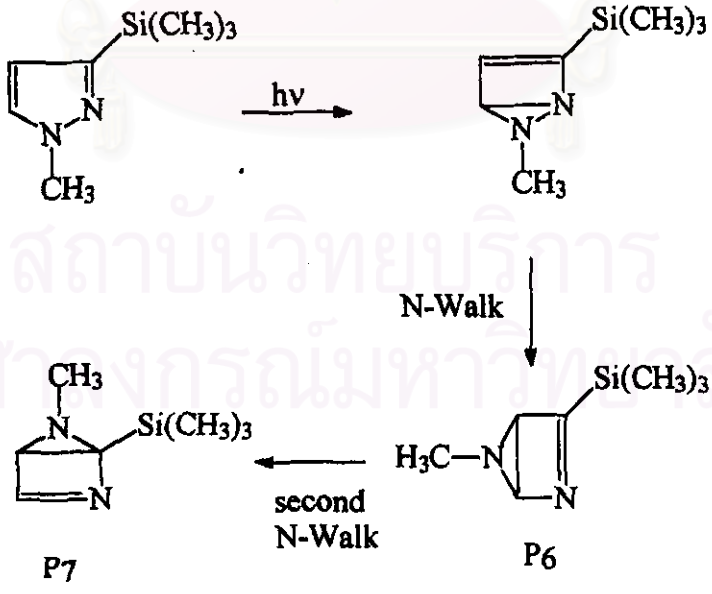


In comparison with the methyl substituent, the trimethylsilyl group has similar electronic effect but different in size. Even though the trimethylsilyl

substituted on C-5 of 1-methylpyrazole enhances P_4, P_6, and P_7 products similar to the methyl substitution on the same position. P_4 pathway seem to be more favorable. This may be because of the larger size of the trimethylsilyl group comparing to the methyl group which would hinder the nitrogen walk over the substitution position.



In the case of 3-(trimethylsilyl)-1-methylpyrazole, the trimethylsilyl substitution has the similar effect comparing to the methyl substitution. Only two phototransposition products were observed, since P_4 & P_7 pathways would lead to the same product, 2-(trimethylsilyl)-1-methylimidazole. However, P_7 pathway be more difficult, perhaps because the second N-walk would lead to a less stable intermediate than P_6 intermediate.



4.2 Proposal for Future Work

The phototransposition reactions of 3- and 5-trimethylsilyl substituted 1-methylpyrazoles have already been investigated. It will thus be interesting to explore the phototransposition of 4-(trimethylsilyl)-1-methylpyrazole in order to complete the study of trimethylsilyl substituted 1-methylpyrazole.

The assumption that 4-(trimethylsilyl)-1-methylimidazole was photoproducts from the photoreaction of both 3-(trimethylsilyl)-1-methylpyrazole and 5-(trimethylsilyl)-1-methylpyrazole should be reconfirmed. And also 3-(trimethylsilyl)-3-(*N*-methylamino)propenenitrile should be synthesized to confirm that it is photocleavage product from the photoreaction of 5-(trimethylsilyl)-1-methylpyrazole. Furthermore, the exact quantum yield of photoproducts should be determined and the mechanism for this kind of photoreaction should be investigated to gain more insight with the phototransposition of trimethylsilyl substituted 1-methylpyrazole.