

SCOPE & OBJECTIVE

Among the plethora of functional groups, the nitronone functionality has secured an important place in the arsenal of synthetic chemists. This was possible largely owing to the brilliant efforts of Huisgen and his group in Munich.

K. N. Houk and his co-workers are responsible for the pioneering investigations of regio selectivity and stereo specificity associated with the 1,3 dipolar cyclo addition.

The discovery of α - chloronitronone and its reactions paved a new avenue in the nitronone - chemistry. The chemistry of α - chloro - nitronones was originated and developed by Prof. A. Eschenmoser and his school (236-238).

Another new vista of the nitronone chemistry is the intramolecular cyclo additions. Such type of reactions have been reviewed by A. Padwa (173) and W. oppolzer (174). Due to these vast synthetic potentiality of the nitronones, a number of natural products and other biologically active substances have been designed and synthesized via nitronone routes (239). Therefore the scope of the nitronone chemistry is abundant. One of the objective of our present work is due to these vast potentiality of "chloro-nitronone", and we have tried to elucidate the cycloaddition patterns of both N- cyclohexyl chloronitronone and N- cyclohexyl 5- hydroxy nitronones with a wide variety of dipolarophiles. Among the numerous nitronones that have been studied so far, majority of them bear at least one C-Substituent.

For the prediction of regio selectivity in 1,3 dipolar cyclo addition reaction, CNDO/2 or ab initio SCF calculations have tremendous scope for our new nitronones. Theoretical work in this field now in progress.

N- cyclohexyl chloro nitronone has been prepared by the treatment of chlorohydrin (240) on an etherial solution of N- cyclohexyl hydroxyl amine along with anhydrous $MgSO_4$.

On the other hand N- cyclohexyl 5- hydroxy nitronone has been prepared by the direct heating of dihydro pyran and N- cyclohexyl hydroxyl amine in dry benzene.

Both the nitronones are very interesting on synthetic point of view because

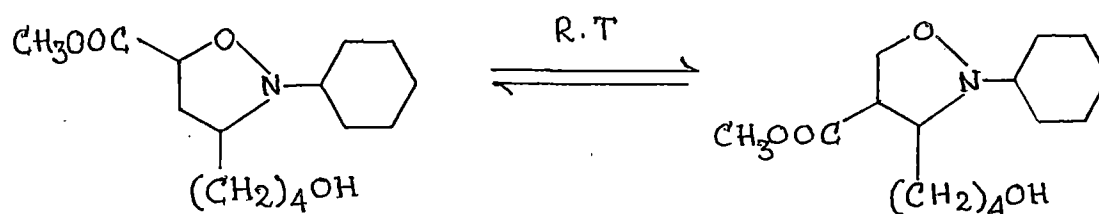
- i) It is quite a new approach from such hemiacetal.
- ii) It has tremendous synthetic potentiality.

The reactions of both N- cyclohexyl chloro nitronone and N- cyclohexyl 5- OH nitronones with moderately electron deficient dipolarophiles are observed to smooth and invariably all the reactions do occur at room temperature in the case of N-cyclohexyl chloro - nitronone, while heating required in the case of N-

cyclohexyl 5-hydroxy nitron, yielding mainly the 5-substituted adducts.

The cycloaddition reactions of N-cyclohexyl chloro nitron with 'acrylonitrile', 'chloro acrylonitrile', 'methyl acrylate', 'ethyl acrylate', 'methyl vinyl ketone' results both 5 and 4 substituted products but the regio selection prefers the 5 substituted adducts over 4 substituted adducts and this has been established from PMR and Mass spectral analysis.

An interesting observation was noticed in the case of Methyl acrylate cycloadducts. It has been found that there is an inter conversion of 5-substituted and 4-substituted cyclo adducts on keeping them at room temperature i.e. cyclo reversion occurs.



N-cyclohexyl 5-hydroxy nitron results mainly 5-substituted cycloadducts, even in the case of ethyl acrylate and acrylonitriles etc. All the additions are found to be stereo specifically cis in nature (245).

N-cyclohexyl chloro-nitron reacts smoothly with the activated acetylenes viz, dimethyl acetylene dicarboxylate, phenyl-methyl propiolate resulting 5-substituted cyclo adducts.

N-cyclohexyl chloro-nitron is equally significant and important for the synthesis of many unnatural cyclic amino acids and lactones.