

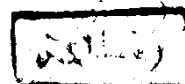
THESIS
ENTITLED
1,3 - DIPOLAR CYCLOADDITIONS

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قالوا

سُبْحَانَكَ لَا إِلَهَ إِلَّا أَنْتَ أَعْلَمُ الْغُيُوبِ
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1,3-DIPOLAR CYCLOADDITIONS

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SUMMARY

SUMMARY

1,3 DIPOLAR CYCLOADDITIONS

$[4n+2]$ π -cyclodimerization of 1-(6-arylpyridazin-3-yl) -3-oxidopyridinium betaines".

The newly synthesized 1-(6-arylpyridazin-3-yl) -3-oxidopyridinium chlorides dimerized readily in a pericyclic process, in the presence of an organic base. The reaction is monitored by i.r. spectroscopy. The ready dimerization and the enhanced reactivity as 1,3-dipole towards a range of 1,3-dipolarophiles (2π & 4π) lead us to measure the kinetic rates of the thermally allowed ($4\pi + 2\pi$) cyclodimerization of the titled betaines in order to see the effect of the 1-(3-pyridazinyl) substituent on the reactivity of the betaine as 1,3-dipole. Dimerization is a function of the energy separation between the interacting frontier molecular orbitals of the betaines under consideration (i.e. the energy gap between HOMO-LUMO of the betaine). Three main factors have been concerned in this study. Concentration, temperature and solvent effects. Study of the effect of concentration of both reactants (i.e. pyridinium salt and triethyl amine) showed that the reaction is 2nd order with respect

to the betaine and zero order with respect to triethylamine

The backward reaction (dedimerization) is 1st order. This supports that the dimerization process is an intermolecular cycloaddition of two betaine molecules while dedimerization (i.e. retrocycloaddition) is an intra-molecular process.

The rate constants have been calculated leading to the computations of the different thermodynamic parameters ΔE^\ddagger , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger .

The dimer formation is favoured at low temperature whereas dedimerization i.e. monomer formation is favoured at relatively high temperature which seems to be completed at 70°C. Solvent polarity has the expected effect where $k_{\text{alcohol}} > k_{\text{chloroform}} \approx k_{\text{1,2-dichloroethane}}$. This indicates that the rate constants increases with increase of the dielectric constant of the solvent used.

Complete dissociation is accomplished only in 1,2-dichloroethane at 70°C. However, the degree of dissociation of the dimer \rightleftharpoons monomer is decreased in ethanol perhaps due to the addition of ethanol molecule to the chromophoric group $C=C-C=O$ via a Michael type of addition.

It is also observed that the change in the ΔG^\ddagger is found to be independent on the change of substituent i.e. 6-phenyl or 6-(4-methylphenyl) and the solvent used. The high negative values of ΔS^\ddagger is in favour with the cyclic transition state, which supports the concerted mechanism. MO's calculation using SCF-PPP quantum mechanical MO. approximate method indicated low HOMO-LUMO energy gap of the interfrontier MO's of the betaine. Sustmann equation gave a large stabilization energy of the transition state set up between 2,6 positions of one molecule and 2',4' positions of the second molecule. Woodward Hoffman general selection rules indicates that one of the betaine molecules react as 1,3-dipole across 2,6 positions (aza allyl anion), with another betaine molecule which is considered as 2π 1,3-dipolarophile across 2',4' positions (i.e. allyl cation). Both HOMO of aza allyl anion (ψ_2) and LUMO of allyl cation (π^*) and LUMO of aza-allyl anion (ψ_3) and HOMO allyl cation (π) interactions are symmetry allowed.

Based on the foregoing data rationalisation of the reactivity of 1-(3-pyridazinyl betaine) is discussed and a likely mechanism has been proposed.

INTRODUCTION

Aim of the work:

3-Hydroxypridine and its 1-substituted 3-oxido-pyridinium betaines fall within the class of 6-membered heteroaromatic betaines possessing a 2π -and / or 4π 1,3 dipoles. The 1,3-dipolar character exhibited by such type of compounds was demonstrated and extensively investigated during last decade by Katritzky *et al*¹. The present investigation deals with the kinetic rates of $(2\pi_s + 4\pi_s)$ thermally allowed cyclodimerization of the newly synthesised 1-(6-arylpyridazin-3-yl)-3-oxidopyridinium betaines. Cyclodimerization reflects the HOMO-LUMO energy differences of the monomeric systems. Meanwhile, MO.Calculations need accurate rate data in order to test the predictive power of 1-(3-pyridazinyl)-3-oxido-pyridinium betaines with the view to correlate the reactivities of such betaines with the previously reported ones¹. So, a survey of literature on the chemistry of 3-hydroxypyridine will be given in the introductory part.

Chemistry of 3-Hydroxypyridine

Hydroxypyridines² (1) are both weak acids and bases and therefore exist as Zwitterions (2). The zwitterions of 2- and 4-hydroxypyridines are known as 2- and 4-pyridones because of their uncharged canonical forms (3) and (4) 2- and 4-hydroxypyridines exist in aqueous solution very predominantly as the oxo-or pyridone form. In aqueous solution the hydroxy and zwitterionic form of 3-hydroxypyridines coexist in comparable amount. 3-Hydroxypyridine behaves as a typical phenol. It gives an intense violet color with ferric chloride and forms a salt (5) with sodium hydroxide which can be alkylated by alkyl halides to give O-alkyl derivatives (6) and acylated by acid chloride to give O-Acyl derivative (7) (cf. scheme 1).