

**STEREOCHEMICAL ASSIGNMENTS OF DIELS-ALDER ADDUCTS OF 6, 6-DIBROMOMETHYL-6-METHYL-2,4-CYCLOHEXADIENONE-MALEIC ANHYDRIDE****RUPESH KUMAR SINGH<sup>1a</sup>, AMOD KUMAR SINGH<sup>b</sup> AND VANDNA YADAV<sup>c</sup>**<sup>abc</sup>Department of Chemistry, A.B.R.P.G.College, Anpara, Sonebhedra, U.P., India**ABSTRACT**

The conformational studies of Diels-alder adducts of 6, 6-dibromomethyl-6-methyl-2, 4-cyclohexadienone-maleic anhydride gives elegant method of determination of the Diels-Alder adduct and also gives the valuable information about Diels-Alder reactions in configurational assignments by using <sup>1</sup>HNMR spectroscopy.

**KEYWORDS :** Diels-Alder, <sup>1</sup>HNMR Spectroscopy, Maleic Anhydride

Configuration means the spatial arrangement of atoms or groups around the asymmetric centre where as conformation denotes any one of the infinite numbers of spatial arrangements of the atom of a molecule that can arise from a rotation about single bond. In case of configuration the spatial arrangements of the atoms of a molecule can be changed only by breaking and making of bonds where as spatial arrangements in conformation are changed simply by rotation of a single bond. Theoretical chemistry now a day's plays a vital role in regeneration of new pharmaceuticals.

Diels- Alder reaction is an addition reaction in which 1, 3 dienes react with olefinic or acetylenic 'dienophile' to form adducts with a six membered hetro-aromatic ring. The reaction is highly stereospecific and is mentioned as a ( $\pi4s+\pi2s$ ) process ( Konuko et al.,1972). Thus the reaction between cyclic diene and dienophile such as maleic anhydride may lead to two stereoisomers with retention of stereochemistry in a concerted mechanism of dienophile. The diene and dienophile approach each other in parallel planes and the orbital symmetry properties of the system allow stabilization of the transition state through bonding interactions between C-1 & C-4 of the diene and the carbon atoms of the dienophile in a six centre arrangement. The mode of addition in the transition states of diene and dienophile determiners its relative orientation. (Williamson. and Hsu, 1970).

The structural and steric rules of Diels-Alder reaction find out most of the fundamental laws of the theory of chemical structure and the reactivity of the organic molecules. Thus to the theoretical & practical point of view it is one of the most general reaction for generating

carboxylic and heterocyclic six-membered ring system.

**EXPERIMENTAL**

6, 6 - d i b r o m o m e t h y l - 6 - m e t h y l - 2 , 4 - cyclohexadienone (96) was obtained by abnormal reimer-tiemann reaction of o-cresol and bromoform in the presence of alkali. (Wenkert and Wovkulich, 1977). This dienone acts as a diene as well as a dienophile. Reaction of this dienone with maleic anhydride at 130-140<sup>o</sup> for about 12-14 hrs gave an adduct(Auksi and Yates, 1981; Yates et al., 1988 and Yates, 1989). Only one spot was observed on TLC plate and IR spectrum and elemental analysis indicate the formation of an adduct (97).

**RESULTS AND DISCUSSION**

<sup>1</sup>HNMR spectrum of the adduct is interpreted as:  $\delta$  1.46 (s, 3H) for- CH<sub>3</sub> protons,  $\delta$  3.5 (m, 2H) for (2 + 3) protons,  $\delta$  4.0 (m,2H) for (1+4) protons,  $\delta$  5.9 (s, 1H) for-CHBr<sub>2</sub> proton,  $\delta$  6.6 & 6.8 (dt, 2H) for olefinic protons. These data support the formation of the adduct but do not provide information to distinguish between the two isomeric adducts 6, 6-Dibromomethyl-6-Methyl-2, 4-Cyclohexadienone-Maleic Anhydride (97a) and (97b). The overall reactions are in Figure 1.

The molecular formula of (97a) & (97b) is C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub> and its melting point (M.P.) is 222-23<sup>o</sup>C and it gives following IR characteristics bands in IR spectra .IR  $\nu_{max}$  cm<sup>-1</sup>-2590b, 1780w, 1710s, 1625w. s=strong, m=medium, w=weak.

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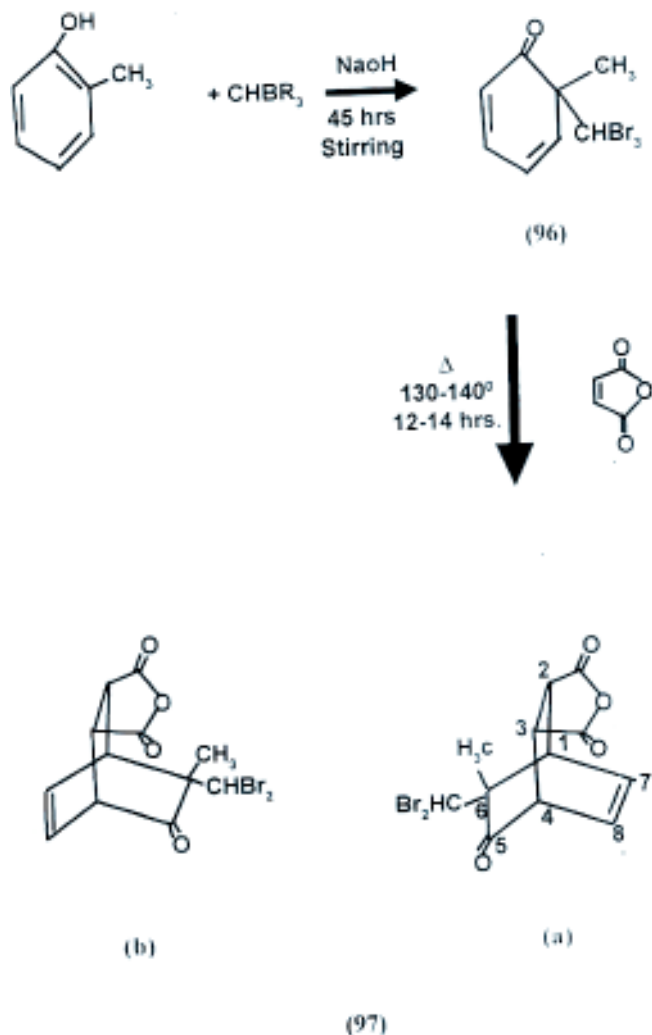


Figure 1: Two (97a and 97b) isomeric adducts of 6-dibromomethyl-6-methyl-2, 4-cyclohexadienone-maleic anhydride

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