MECHANISM OF THE STEREOISOMERIC CONVERSIONS OF NITROENAMINES CONTAINING A N—H BOND IN CHLOROFORM—METHANOL MIXTURES

V. I. Bakhmutov and E. I. Fedin

The rotation around the C=C bond (Z,E-isomerization) of enamines containing a tertiary amino group takes place by a thermal mechanism through a polar transition state [1].

\[ \text{C} = \text{C} \rightarrow \text{C} = \text{C} \]

The stereoisomeric conversions of enamines containing a secondary amino group may have a more complex mechanism due to the participation of the N—H bond in the reaction, the Z,E-isomerization of enamino ketones and enamino ethers containing a N—H bond being accompanied by proton-exchange reactions between the molecules of the compounds being isomerized [2, 3], while in proton-donor solvents the solvent molecules also participate in the exchange [4]. Consequently, the Z,E-isomerization of such compounds requires detailed study.

In this investigation we have studied the isomeric conversions in a proton-donor solvent of enamines containing a N—H bond, using as examples the nitroenamines (I) and (II)

\[ \text{R—N} / \text{CO}_2\text{CH}_3 \rightarrow \text{R—N} / \text{CO}_2\text{CH}_3 \]

As solvents we chose the mixtures CD₃OD—CDCI₃ and CH₃OH—CDCI₃ in a ratio of 1:1 by volume, and we used dynamic PMR [5] as the method for studying the isomerization kinetics. Methanol was mixed with chloroform to increase the solubility of the compounds being studied and to increase the difference in the chemical shifts of the COOCH₃ groups in the Z- and E-isomers \((\Delta\delta_{\text{COOCH}_3})\), \(Z,E = 6.6\) Hz for (I) and \(5.8\) Hz for (II)). The lifetime of the stereoisomers \((\tau_{Z,E})\) was determined by a total analysis of the line shape of the signals from this group in the PMR spectra according to a standard program for two-center exchange [5]. On studying the temperature dependence of the PMR spectra under conditions of slow Z,E-transitions it was found that the isomeric equilibrium constant of enamine (II) \(K_E = [Z]/[E]\) (it was determined by integrating the CH signals, the difference in the chemical shifts of whose isomers is equal to \(47.5\) Hz) depends appreciably on temperature. Thus, the fraction of the Z-isomer increases with a decrease in the temperature of the specimen (Fig. 1). The relationship observed was therefore taken into account when calculating \(\tau_E\) and \(\tau_Z\). In the case of enamine (I) this relationship is less well-defined; with a change in the temperature of the specimen from 14 to 51°C the value of \(K_E\) changes from 1.7 to 1.5. After calculating \(\tau_{Z,E}\) from the temperature dependence of this parameter by the method of least squares the activation parameters of the Z,E-isomerization were found (Table 1). As follows from the data obtained on changing from enamine (I) to (II), i.e., with an increase in the electron-donor strength of the substituent \(R\), the rate of the isomeric transitions \((1/\tau)\) increases, while the quantities \(E_g\), \(\Delta H\), \(\Delta S\) and \(\Delta G\) decrease, which corresponds to a greater stability of the activated complex in case (II). This fact enables us to represent the isomerization of (I) and (II) within the framework of a thermal mechanism [1]. For the example of aromatic nitroenamines of

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR.


1446 0568-5230/81/3008-1446$07.50 © 1982 Plenum Publishing Corporation
Temperature dependence of the isomeric equilibrium constant $K_e = [Z]/[E]$ of enamine (II) in CD$_3$OD–CDCl$_3$ solution in Arrhenius coordinates.

Fig. 2. Relationship between the parameters $\Delta H^\#$ and $\Delta S^\#$ for $Z,E$-isomerization of (II) in CD$_3$OD (1), CD$_3$OD–CDCl$_3$ (2); that of (I) in CD$_3$OD (3) and CD$_3$OD–CDCl$_3$ (4).

Type (I) $Z,E$-isomerization has previously been detected involving a preliminary and kinetically controllable stage of ionization of the N–H bond and a subsequent rapid rotation into the mesomeric ion being formed (a dissociative mechanism), this being observed in solutions of basic aprotic solvents [6]. In spite of the reverse effect of a substituent being characteristic of such isomerization, to confirm the conclusion of a thermal mechanism for the isomerization of the nitroenamines being studied in methanol solution it is necessary to make certain that the mechanism of the stereoisomeric conversions does not alter during the transition from (I) to (II). As follows from Fig. 2, a satisfactory linear correlation is observed between the parameters $\Delta H$ and $\Delta S$, which indicates the existence of a compensation.