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VINYLAMINES - XII[1]

EQUILIBRIUM IN ENAMINES FROM 3-SUBSTITUTED CYCLOHEXANONES: HIGH SELECTIVITY OF β-NITROSTYRENE TOWARDS THE Δ_6 ISOMERS

E.Valentin, G.Pitacco and F.P.Colonna
Istituto di Chimica, Università di Trieste
34127 Trieste, Italy

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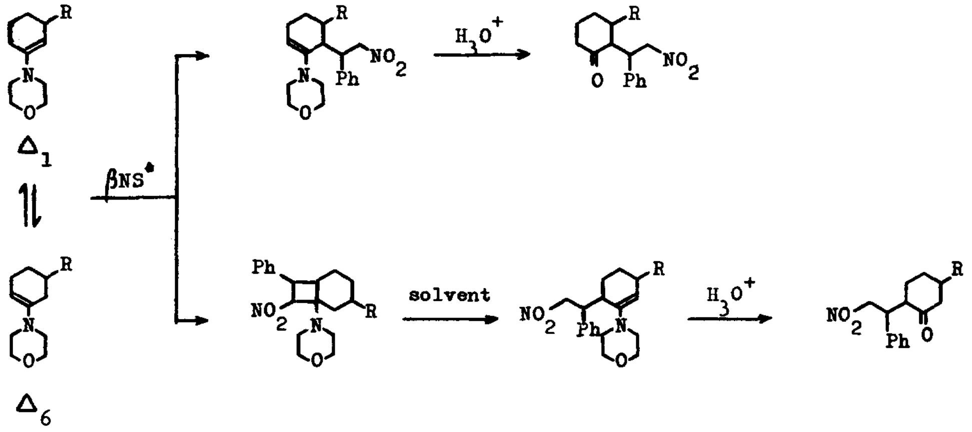
The problem of the equilibrium between the two isomeric forms in an enaminic mixture has been subject of numerous discussions. It has been demonstrated that in the case of enamines derived from acyclic ketones, this equilibrium exists[2]. In the 2-alkyl cyclohexanone enamines it can be attained only by adding an acidic catalyst[3] or by raising the temperature[4,5]. Few data are available about the 3-substituted cyclohexanone enamines and they have been obtained under reaction conditions which do not seem, in our opinion, to be strictly non-equilibrating[6,7]. Our purpose was to define whether or not an equilibrium exists also in enamines from 3-alkyl and 3-aryl cyclohexanones. We have chosen β-nitrostyrene since it reacts quantitatively with some trisubstituted enamines[8,9] to give enaminic or cyclic adducts, which easily undergo hydrolysis (Scheme).

Scheme



R = Me; Ph

*The reactions were carried out at 5°C, for 72 hr, in anydrous ether.

Actually our experimental data, obtained under non-equilibrating conditions, clearly indicate that there is a deviation between the percentages of the adducts thus obtained and the composition of the parent enamines (Table).

Table

		% of vinylic proton[6] (N.M.R.)	Yields (%) of adducts
R = Me	Δ_1	45	20
	Δ_6	55	80
R = Ph	Δ_1	~ 100	20
	Δ_6	~ 0	80

This result can be explained by admitting the existence of a rapid equilibrium between the Δ_1 and Δ_6 forms. The evident high selectivity of the olefine is interpreted in terms of steric and stereoelectronic effects. In fact an antiparallel attack of the reagent on both conformers of Δ_1 requires a too high activation energy. Since the reaction is under kinetic control, the most favoured antiparallel attack is that on the conformer of Δ_6 in which the substituent is equatorial.

The configurational and conformational problems involved are in course of study.

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