Using Empirical Rules from ^{13}C NMR Analysis to Determine the Stereochemistry of the Epoxide Located at the 5,6-position of Decalinic Systems

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Abstract: An empiric rule derived from the analysis of the ^{13}C NMR spectral data, allowed us to determine 5,6-epoxide stereochemistry on decalinic systems and a discussion of the scope and limitations of this rule and its extension to other carbon squeletons, is presented.

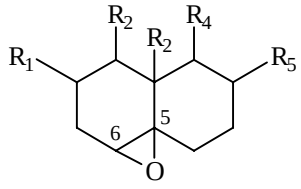
Introduction

^{13}C NMR and ^{1}H NMR techniques are the most convenient methods for the elucidations of the oxirane ring stereochemistry in condensed policyclic systems, and have been widely used in the research of epoxides from natural sources [1-3].

Very often, however, the methods used consider mainly the effects of the oxirane ring on the γ carbons [4-6].

Results and Discussion

From the analysis of the ^{13}C NMR data of a set of synthetic epoxides angularly substituted and placed on the C_5-C_6 position of decalin systems of known relative configurations; we could stablish an empirical correlation between the chemical shift difference of the oxirane carbons and the relative configuration of the epoxide. Therefore, using these chemical shift differences it is possible to predict the α or β orientation of the epoxide, that is, *trans* or *cis* stereochemistry of the epoxide relative to the C_{10} substituent (R_3).



Computing for each epoxide: $\Delta\delta_{(epoxide)} = \delta_{C-5} - \delta_{C-6}$, the subtraction between the ^{13}C NMR chemical shifts of both oxirane carbon signals, predicts:

$$\Delta\delta\ \alpha\text{-epoxide} > 5 \text{ ppm}$$
$$\Delta\delta\ \beta\text{-epoxide} < 3.8 \text{ ppm}$$

Besides, we will present a discussion of the scope and limitations of this rule, its possible extension to other carbon skeletons and the comparative analysis with those results obtained from the existent semiempirical calculation systems [5,6].

Experimental

The epoxides were synthesized from substituted α- tetralones through a sequence involving a Birch reductive alkylation followed by the reduction and epoxidation with *m*-CPBA in heterogeneous phase.

The determinations of the ^{13}C NMR spectra were realized in $CDCl_3$ solutions using standard conditions.

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References and Notes

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