CHEMISTRY OF N-OXIDES : FURTHER DEVELOPMENTS

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The Polonovski reaction discovered in 1927 is a very useful biomimetic reaction. The replacement of acetic anhydride of the genuine reaction with trifluoroacetic anhydride allowed this "modified Polonovski reaction" to be used in achieving various syntheses of complex natural biomolecules.

After recalling some previous main points of this research : mechanism, reactions of elimination and/or fragmentation, applications to the synthesis of ervatamine-type compounds, vinblastine-type compounds, demonstration of the biomimetic character of this reaction, a description of some new applications of this reaction will be made.

A - MASKED DIHYDROPYRIDINES :

Dihydropyridines constitute important building blocks for the elaboration of various nitrogen-containing biomolecules. The use of the modified Polonovski reaction has allowed H.-P. Husson and co-workers to prepare, from conveniently substituted tetrahydro-pyridines, dihydropyridinium salts which are trapped with cyanide ions and which constitute masked dihydropyridines amenable to various syntheses of alkaloids. Various examples will be given of the usefulness of this reaction. Enantioselective syntheses will also be described using nor-ephedrine as a "chiral inducer".

B - REACTIVITY OF N-OXIDES IN STRONGLY BASIC MEDIA :

This reaction developed by R. Beugelmans and co-workers consists of treating convenient N-oxides with a strong base. An azomethine ylide, in equilibrium with the corresponding biradical, is obtained. Trapping of these transcient intermediates with non-activated olefins led to pyrrolidine or piperazine derivatives.

Various examples of the possible applications of all these new reactions will be given.