Highly Stereoscopic Differentiation of 5-Formyl-5-methyl-1-pyrazolines. Preparation and Characterization of Stable Carbolinamines (Amino Hemiacetals)

A. F. Noels,* J. N. Brauman, A. J. Hubert, and Ph. Truysser

Department of Organic Chemistry, University of Louvain, Louvain, Belgium

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The unstable 5-formyl-5-methyl-2-pyrazolin-3-one, prepared in situ by a 1,2-dipolar addition of dimethyl acetylenedicarboxylate (maleimide) to diazo esters, dimers in a highly specific way to give 4, which are stable carbolinamines. Surprisingly, the latter show no equilibration with the monomeric pyrazolines in solution, even at 50°C in MeOH, but they show a characteristic rearrangement of 4 to 5 occurs with retention of configuration at the reacting center, as established by nmr spectroscopy.

It has been clearly recognized for a long time that the formation of hydrazones, imines, oximes, etc., is a two-step reaction, a carbamino being an obligatory intermediate,1 hence a reaction of (1) + (2) and (1) + (3) (also called hemimel or amino hemiacetal) has attracted much less attention, although several natural compounds have recently been recognized to possess a stable amine hemiacetal function.5 From a synthetic point of view, the exceptions of halogen stabilized molecules, or derivatives of strained cyclicophane,4 the differentiation of five-membered heterocycles with a formy group to an endocyclic NH constitute to our best knowledge the only systematic attempts to the stabilization of amino hemiacetals, and in this case, never was the function clearly and fully characterized, because of nonresolved mixtures and of a dimers-monomers equilibrium in solution. We now report the highly stereoscopic characterization of stable carbolinamines from the stereospecific differentiation of substituted 5-formyl-5-pyrazolines.
Noels, Ibrahim, Hubert, and Tneyrié

Scheme I

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\begin{align*}
\text{Scheme II} \\
\text{Scheme III}
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Discussion on the synthesis and properties of 2,4-dimethyl-4-oxo-2,3-oxazolidinone.

Dimerization of 5-Formyl-5-methyl-1-pyrroline. One on a Buehler HFX 60 instrument at 22.60 MHz. All chemical shifts are measured in parts per million (δ) from Me4Si or HMDSD. The 1H and 13C NMR spectra were assigned by a combination of 2D NOE experiments and 2D ROESY experiments. The assignments and the structure of the compound, 2,4-dimethyl-4-oxo-2,3-oxazolidinone, is consistent with the NMR and IR characteristics of the compound. The structure of the compound is further supported by the COSY and HSQC experiments.

References and Notes