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Conformational Study of some novel Methoxy Half-Analogues of Michler's Ketone by NMR

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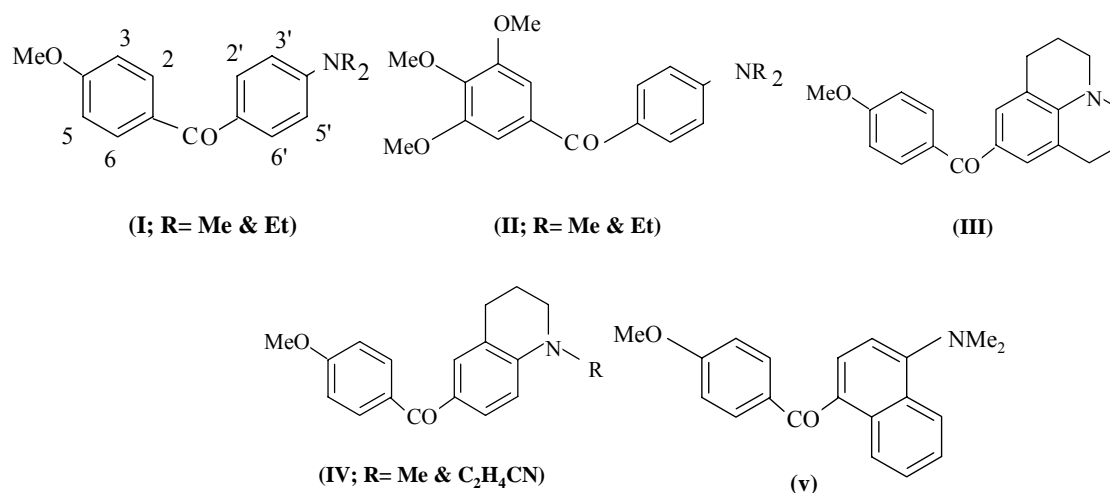
Abstract

One series of half-analogues of Michler's ketone containing one or more terminal methoxy substituents with variable tertiary amino groups have been used in this study. NMR spectral results for the parent ketones confirm earlier findings that ortho proton shifts are apparently independent from steric effects in derivatives of Michler's ketone because the ring current and carbonyl-induced shifts are self-canceling.

Keywords: Conformational study; Michler's Ketone; NMR Spectroscopy; Proton Shift; Steric Effect; Ring Current; Carbonyl-induced shift; Tertiary amino groups.

1. Introduction

Recently, a comprehensive range of analogues and derivatives of Michler's ketones (I-V) has been synthesized and their electronic absorption spectra studied [1]. In the present work, their NMR spectral characteristics have been studied.



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NMR spectroscopy has been used to investigate the conformational preference of substituted benzophenones, especially those containing ortho substituents [2]. In this connection, some derivatives of Michler's ketone have also been examined [3]. Owing to the proximity of the two aromatic rings, shielding by the ring current of adjacent nucleus on the ortho positions is a function of the molecular conformation.

2. Experimental

^1H NMR spectra were recorded for the present ketones in deuterio chloroform by the Physico-Chemical Measurements Unit (PCMU), Harwell, on Varian HA-100D (100MHz) and HR-220 (220 MHz) spectrometers at ambient probe temperatures (308 to 313 °K at 100 MHz, 303 °K at 220 MHz). The resulting ^1H chemical shifts are listed in Table 1.

Table 1

H Chemical shifts (σ) in some methoxy half-analogues of Michler's ketone.

Ketones/ Chemical shifts	I; R= Me	I; R= Et	III	IV; R Me	IV; R= C ₂ H ₄ CN	II; R= Me	II; R= Et	V
2-H	7.75	7.7	7.7	7.7	7.7	7	6.95	7.8
3-H	6.8	6.75	6.85	6.85	6.7	-	-	7.1
5-H	6.6	6.75	6.85	6.85	6.7	-	-	7.1
6-H	7.75	7.7	7.7	7.7	7.7	7	6.95	7.8
2'-H	7.75	7.7	7.7	7.7	7.7	7.8	7.75	7.8
3'-H	6.8	6.75	-	-	-	6.7	6.6	7.1
5'-H	6.8	6.75	-	6.85	6.7	6.7	6.6	-
6'-H	7.75	7.7	7.7	7.7	7.7	7.8	7.75	-
O-CH ₃	3.85	3.8	3.81	3.9	3.85	3.85	3.8	3.8
N-CH ₂ - or N-CH ₃	3.05	3.25	-	3.05	3.15	3	3.4	3
N-CH ₂ CH ₃ or N-CH ₂ CH ₃	-	1.15	-	-	1.1	-	1.15	-
β -CH ₂	-	-	1.9	2	2	-	-	-
α or γ -CH ₂	-	-	3.25/2.75	3.4/2.8	3.55/2.7	-	-	-

3. Results and Discussion

The bonding interaction between the π -electrons of the aromatic ring and the π -electrons of the carbonyl group (conjugation) is well recognized in aromatic ketones [4]. The percentage of double bond character induced by conjugation into the C_{Ar}-CO bond raises the energy barrier to internal rotation about this bond and the rotation becomes thermodynamically and not kinetically restricted at room temperature. Conformations where the aromatic ring and the carbonyl group are coplanar (i.e. maximum π - π overlap) become strongly preferred whenever structurally possible [4]. In general, there are two opposing effects which govern the molecular conformation of aromatic ketones: (a) conjugative interaction between the benzene rings and the carbonyl group, which is at a maximum when the angle (ϕ) between the C-CO-C plane and the benzene ring plane is zero, and (b) non-bonded repulsive interactions which tend to keep ϕ above minimum. The conjugation of the nitrogen atoms with the aromatic rings in the ketones listed in Table may influence factor (a) above, and the conformations in solution of such compounds are of interest both intrinsically and in complementing analogous information for this type of ketone. The strong anisotropy of magnetic susceptibility of benzene rings (rationalized by the concept of π -electron ring currents) should lead to strongly ϕ -dependent ^1H NMR Chemical shifts.

It can be seen from Table that the chemical shifts of protons ortho to carbonyl appear to be remarkably insensitive to variations in substitution patterns elsewhere. Only in the case of trimethoxy derivatives are the 2-H shifts changed from $\delta 7.7$ to $\delta 7.0$, owing to the influence of the adjacent methoxy groups. It is clear that the variations in the conjugative ability of terminal

substituents are not reflected in the chemical shifts of the o-protons and it might be concluded that ϕ remains essentially constant. Although this conclusion is not unreasonable in the case of the present series of ketones in which steric effects are minimal, it has previously been shown for a group of analogous derivatives of Michler's ketone that the ring current and carbonyl-induced shifts are largely self-canceling [3]. The previous work [3] suggested that conjugative interaction between the terminal nitrogen atoms and carbonyl group has little effect on the conformation of the compounds studied. The close similarity between the present data and that of the related derivatives of Michler's ketone indicates that the same conclusion is valid here.

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