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Keto–enol and enol–enol tautomerism in trifluoromethyl-β-diketones

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Abstract

The keto–enol (K$\rightleftharpoons$E) and enol–enol (E$\rightleftharpoons$E) equilibria of a variety of trifluoromethyl-β-diketones were investigated using ^{1}H, ^{13}C, ^{19}F NMR spectroscopy, infrared spectroscopy and ultraviolet-visible spectrophotometry in nonpolar solvents. In general, NMR, IR and UV spectral evidence indicates that trifluoromethyl-β-diketones exist as mixtures of two chelated *cis*-enol forms in nonpolar media. Infrared spectroscopy and ultraviolet spectrophotometry show the E$\rightleftharpoons$E equilibrium lies in the direction of the enol form which maximizes conjugation in most cases. Exceptions are noted and discussed.

Keywords: β-Diketone; Tautomerism; Enol; ^{19}F NMR; Chelated-OH; Enone

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1. Introduction

In earlier work we reported the regioselective synthesis of fluorine and trifluoromethyl containing β-diketones and their conversion to various heterocycles [1]. While monitoring these cyclizations with ^{19}F NMR, we noted, as expected, the predominance of enolic forms of the β-diketones. Notable exceptions were the 2-fluoro derivatives and β-diketones with large alkyl groups substituted at C-2. These compounds shown in Fig. 1 exhibit only the keto form in $CDCl_3$ [2].

Since fluorine in the 2-position of β-diketones has such a dramatic effect on the keto–enol equilibrium ($K_{k\rightleftharpoons e}$), we decided to explore the effect of fluorine substitution in other positions. In this paper, we describe the preparation and examination of a number of β-diketones where a $-CF_3$ group is a terminus. In these cases the equilibrium potentially involves the diketone and two chelated, hydrogen-bonding enols, a and b, Fig. 2.

While non-chelated enols may be considered, these are observed in rare instances. In non-hydrogen bonding solvents, the enols which can hydrogen bond intramolecularly are the more stable [3].

Analyzing the system diagrammed in Fig. 2 is especially challenging since isomers a and b may be interconverted by intramolecular movement of a hydrogen atom from one oxygen to another over a small distance. In several special cases the equilibrium a$\rightleftharpoons$b has been studied using NMR, IR and UV data [4] (see Table 1).

In the present paper these spectral techniques are applied to a wider variety of trifluoromethyl-β-diketones, including aliphatic, aromatic and cyclic examples. The results, $K_{keto\rightleftharpoons total\ enol}$ ($K_{k\rightleftharpoons e}$) and $K_{enol\ a\rightleftharpoons enol\ b}$ ($K_{a\rightleftharpoons b}$), determined by each of the three spectroscopic methods are compared and trends and differences discussed.

2. Results

2.1. β-Diketone synthesis

Table 2 shows trifluoromethyl-β-diketones selected for the keto–enol and enol–enol equilibrium study. These include commercially available diketones (**1a–d**, **1g**, **1h** and **1u**) and those prepared by literature methods [1,2,10]. For comparison purposes, two nonfluorinated diketones, **1w** and **1x**, were included in the investigation.

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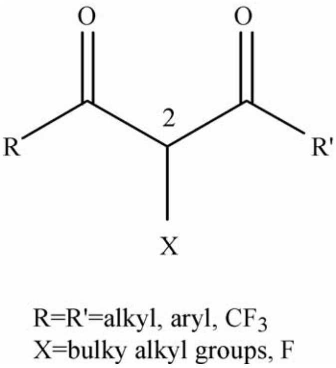


Fig. 1. β-Diketones, which exhibit the keto form.

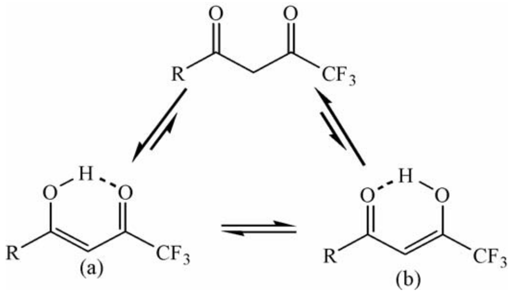


Fig. 2. Keto and chelated enol forms.

2.2. Spectroscopic studies

2.2.1. NMR spectroscopy

In Table 3 are presented ^{1}H, ^{13}C and ^{19}F NMR data. Tautomeric assignments are based on work previously reported in the literature [5].

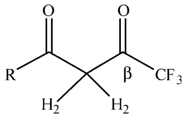
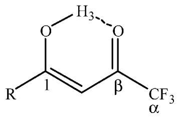
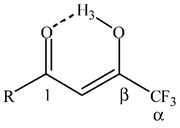
2.2.2. Infrared spectroscopy

Infrared spectroscopy was used to detect the various enol and keto species of selected trifluoromethyl-β-diketones present and to determine the direction of enolization. Band assignments in the IR spectra of β-diketones that clearly distinguish the keto and enol forms a and b are based on the infrared data in Table 1 [6,7b,11]. Our results are reported in Table 4.

2.2.3. Ultraviolet–vis spectrophotometry

As indicated in Table 1, UV–vis spectrophotometry in some cases may also provide resolution of the enol forms [6b,7]. Consequently, a wider variety of trifluoromethyl-β-diketones was examined by UV–vis spectrophotometry. The data for our series of trifluoromethyl-β-diketones are presented in Table 5. The λ_{max} values are consistent with carbonyl compounds that have extended conjugation. Where available, λ_{max} values for both the keto and enol tautomers are presented. In several cases, resolution of the enols was observed.

Table 1
Spectral Information for trifluoromethyl-β-diketones

Spectral Method	Units	R	Keto 	Enol a 	Enol b 
NMR[a]	δppm	Alkyl/Aryl	^{1}H: $H_2 \sim 3.90$, ^{19}F: $\sim -80– -84$, ^{13}C: $C_\beta > 200$	^{1}H: $H_3 \sim 15–18$, ^{19}F: $\sim -73– -78$, ^{13}C: $C_\beta \sim 170$,	^{1}H: $H_3 \sim 12–15$, ^{19}F: $\sim -73– -78$, ^{13}C: $C_\beta \sim 160$,
	J (Hz)			$^{1}JC_{\alpha\text{-F}} \sim 285$ $^{2}JC_{\beta\text{-F}} \sim 34–36$	$^{1}JC_{\alpha\text{-F}} \sim 270$ $^{2}JC_{\beta\text{-F}} \sim 32–36$
IR[g]	(cm^{-1})	Alkyl	1700–1790[b]	1580–1640[c]	1650–1700[c]
		Aryl	1687–1689[b]	1595–1620[c]	1650–1678[d]
		Heteroaromatic	1700–1780[b]	1590–1620[c]	1650–1680[e]
		Cyclic	1700–1780[b]	1550–1640[f]	1655–1700[f]
UV[h,i]	(nm)	Alkyl	180–225[j]	270–>300	240–270
		Aryl	225–265	>300	270–300
		Heteroaromatic	230–290	>300	240–>300
		Cyclic	190–260[j]	>300	230–290

[a] Ref. [5].
[b] Unconjugated C═O.
[c] Chelated C═O.
[d] Chelated benzoyl.
[e] Chelated aroyl.
[f] Ref. [6b].
[g] Refs. [6,7].
[h] Unless noted, bands listed are $\pi \rightarrow \pi^*$ transitions.
[i] Refs [8,9].
[j] $n \rightarrow \sigma^*$ transition.