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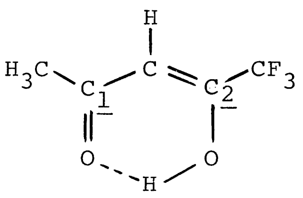
A CARBON-13 NMR STUDY OF THE DIRECTION OF ENOLIZATION OF TRIFLUOROACETYLACETONE

Jun NIWA, Mitsuru YAMAZAKI,* and Tsugio TAKEUCHI*
College of General Education, Nagoya University, Chikusa,
Nagoya 464
*Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Chikusa, Nagoya 464

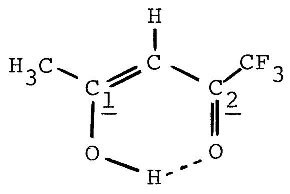
Solvent shifts of the chelated carbonyl carbons of trifluoroacetylacetone reveal the predominance of the enol form which is enolized toward the trifluoroacetyl group.

In the course of IR,[1,2] UV,[3] and NMR[4,5,6] studies which were performed in examining the direction of enolization of unsymmetrically substituted β-diketones, Park, Brown, and Lacher suggested on the basis of IR spectra that trifluoroacetylacetone (TFAA) is enolized toward the trifluoroacetyl group.[1] ^{1}H NMR spectra, however, have not yet been available to resolve the problem,[6] presumably because they provide only indirect information about the structural change. In contrast, ^{13}C NMR spectra can provide more direct insights into the bonding situation.[7]

Thus, we have investigated which structure is dominant among possible enol forms, [1], [2], and [3], of TFAA in nonpolar solvents, by measuring the ^{13}C chemical shifts of the chelated carbonyl carbons, $C_{\underline{1}}$ and $C_{\underline{2}}$, in several solvents.



[1]



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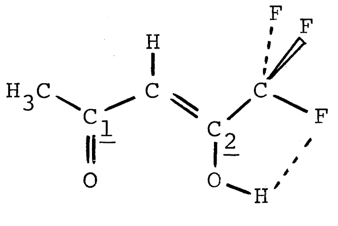


[3]

Signals of $C_{\underline{1}}$ and $C_{\underline{2}}$ were assigned by the comparison of ^{13}C, ^{19}F spin coupling

Table 1. Solvent Effects on ^{13}C Chemical Shifts (δ) of Chelated Carbonyl Carbons[a)]

	i) Salicylaldehyde		ii) Acetylacetone	iii) Dibenzoylmethane
Solvent	C_1	C_2	C_1, C_2	C_1, C_2
C_6D_{12}	196.2	161.6	190.8	— b)
$CDCl_3$	196.2	161.4	190.9	185.8
Acetone-d_6	198.0	162.3	192.3	186.5
Dioxane-d_8	196.7	161.4	—	—
DMSO-d_6	192.0	160.6	191.4	185.6

iv) Trifluoroacetylacetone

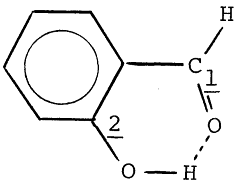
Solvent	C_1	C_2
C_6D_{12}	193.6	177.4
$CDCl_3$	194.4	175.9
Acetone-d_6	196.8	175.6
DMF-d_7	193.2	175.5
DMSO-d_6	189.2	174.9

a) The ^{13}C chemical shifts, δ, were measured using TMS as an internal reference. The proton-decoupled natural abundance ^{13}C FT NMR spectra were obtained with a Varian XL-100-15 with a VFT-100X at 25.2 MHz at 27±2°C. Concentrations of the samples were maintained at 10.0±0.5 Mol%. Measurement conditions: spectral width, 5000 Hz and 6000 Hz; acquisition time, 0.4 sec; number of data points, 4096 and 3686; pulse width, 70 μsec.

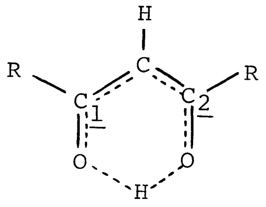
b) DBM was not soluble in C_6D_{12} enough to detect the ^{13}C signals.

constants. The ^{13}C NMR spectra showed that TFAA exists almost completely in the enol form in nonpolar solvents.

In order to obtain the preliminary information about the solvent effects on the chelated carbonyl carbon signals, we have measured solvent shifts of the carbon signals in salicylaldehyde [4], and symmetrically substituted β-diketones, acetylacetone (AA) and dibenzoylmethane (DBM) [5]. The chemical shift values obtained are listed in Table 1. As Fig. 1-(a) shows, in the case of salicylaldehyde, the chemical shift of C_1 showed the most marked upfield shift in DMSO-d_6 compared with that in C_6D_{12}, whereas that of C_2 was not seriously changed. This can be interpreted as showing that the intramolecular hydrogen bonding of salicylaldehyde is cut off by forming the intermolecular hydrogen bonding with a DMSO molecule.[8)] In the case of

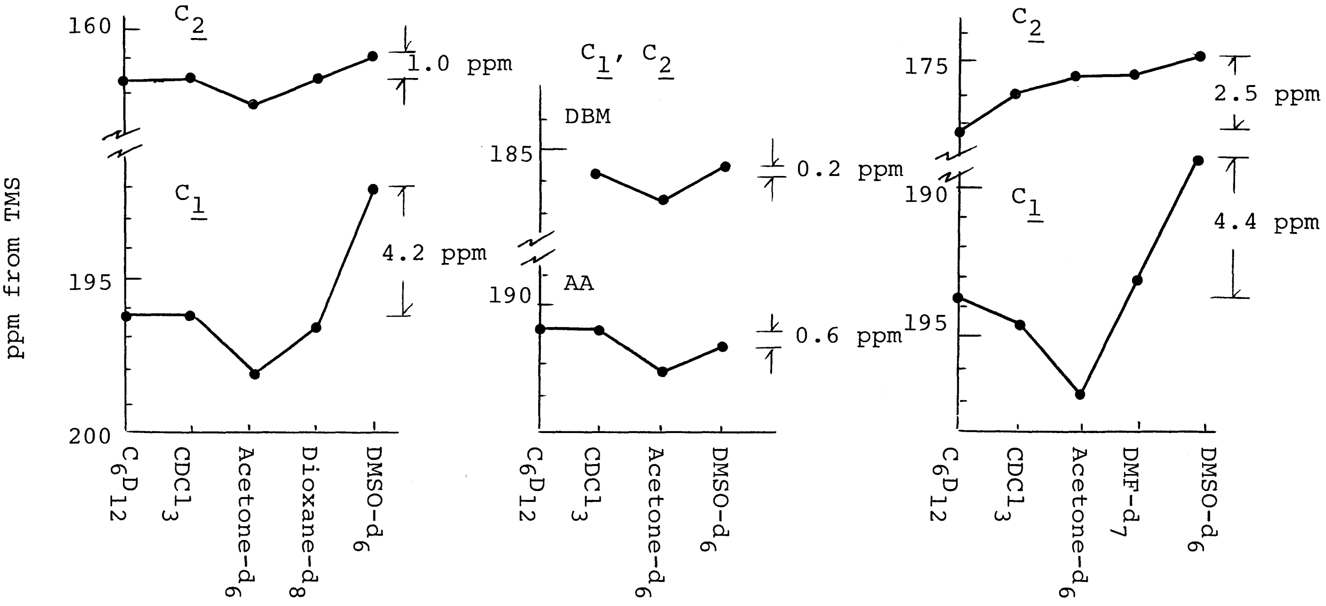


[4]



R: CH_3 or C_6H_5

[5]



a) Salicylaldehyde b) Acetylacetone and Dibenzoylmethane c) Trifluoroacetylacetone

Fig. 1. Solvent Shifts of Chelated Carbonyl Carbon Signals.

AA and DBM [5], as shown in Fig. 1-(b), the chemical shifts of $C_{\underline{1}}$ and $C_{\underline{2}}$ were not largely changed in any solvents; this fact may be explained by assuming that the intramolecular hydrogen bonding is not cut off even by a DMSO molecule, because the chelate-ring is stabilized by the conjugatively electron-donating substituents, the methyl or the benzoyl group.

Table 1-(iv) and Fig. 1-(c) show the solvent shifts of the chelated carbonyl carbon signals of TFAA. As is clearly seen in Fig. 1-(c), the chemical shift of $C_{\underline{1}}$ showed the marked upfield shift in DMSO-d_6 compared with that in C_6D_{12}, while that of $C_{\underline{2}}$ was not seriously changed; this observation is quite similar to that for salicylaldehyde, and can be interpreted as demonstrating that the intramolecular hydrogen bonding, $-\overset{|}{C}_{\underline{1}}=O\ldots H-O-\overset{|}{C}_{\underline{2}}=$, is cut off by a DMSO molecule. This implies that the chelate-ring is weakened by the CF_3 group, a strongly electron-withdrawing substituent.

If we assume form [3] which was suggested by Park et al.,$^{1)}$ the chemical shifts of both $C_{\underline{1}}$ and $C_{\underline{2}}$ may not largely be changed in DMSO-d_6 compared with those in C_6D_{12}, because $C_{\underline{1}}$ resembles the carbonyl carbon of acetone, the solvent shift of which is small in DMSO-d_6 compared with that in C_6D_{12},$^{9)}$ and because $C_{\underline{2}}$ is the enolized carbon, as well as in the case of enol form [1], even though it forms the intramolecular hydrogen bonding with the fluorine atom.

Therefore, it is concluded that TFAA exists dominantly in the enol form [1] in nonpolar solvents, which is enolized toward the CF_3 group.

References and Notes

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9) Unpublished data: The chemical shift of the carbonyl carbon of acetone, δ, was 203.9 in C_6D_{12} and 205.9 in DMSO-d_6.

* Present address of M. Y.; School of Pharmacy, Hokuriku University, Kanagawa-cho, Kanazawa 920-11.

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