

Received: January 12, 1990; accepted: March 2, 1990

$^{19}\text{F}$ - AND  $^1\text{H}$ - NMR SPECTRA OF CYCLIC FLUORO- AND TRIFLUOROMETHYL-  
KETONES

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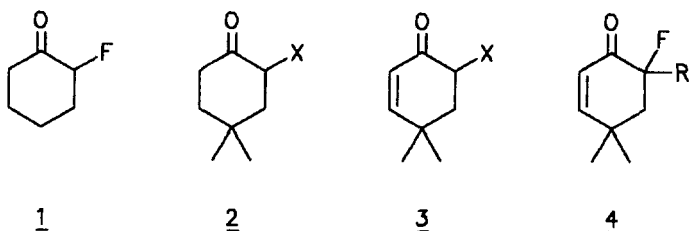
SUMMARY

The  $^{19}\text{F}$ - and  $^1\text{H}$ -NMR spectra of several 2-X-cyclohexanones and 6-X-cyclohex-2-enones (X = F,  $\text{CF}_3$ ) are reported and discussed.

INTRODUCTION

Fluorine-19 nuclear magnetic resonance spectroscopy is a well established method for structural elucidation and conformational analysis of fluoroorganic compounds [1,2], stereochemical aspects of  $^2J_{\text{FH}}$  - and  $^3J_{\text{FH}}$  - values [3,4] being well understood for several types of organic molecules. It is of interest that with the exception of some reports on 2-fluorocyclohexanone [5,6] and 2-fluorocyclooctanone [7], cyclic  $\alpha$ -fluorocarbonyl compounds have not been investigated in detail. Very recently N-fluoropyridinium salts have been suggested by *Umamoto* [8,9] as mild and selective reagents for the preparation of  $\alpha$ -fluoro ketones from silyl enol

precursors. We have also used this method and extended its scope in preparing 6-fluorocyclohex-2-enones from cyclohexadienyloxy-trimethylsilanes, and now report detailed  $^{19}\text{F}$ - and  $^1\text{H}$ -NMR data of 2-fluorocyclohexanones 1 & 2a and of 6-fluorocyclohex-2-enones 3a, 4a & 4b. In addition we report the  $^{19}\text{F}$ -NMR spectra of the corresponding trifluoromethyl-ketones 2b & 3b and - for comparative purposes - their  $^1\text{H}$ -NMR spectra as well as those of the parent (unsubstituted) ketones 2c & 3c.



a: X = F  
b: X = CF<sub>3</sub>  
c: X = H

a: R = CH<sub>3</sub>  
b: R = CH<sub>2</sub>C(Me)=CH<sub>2</sub>

## RESULTS AND DISCUSSION

The  $^{19}\text{F}$ - chemical shifts (in ppm relative to CFCl<sub>3</sub>), the  $^1\text{H}$ - chemical shifts (in ppm relative to TMS) and the coupling constants (in Hz) of 3.10<sup>-1</sup>M CDCl<sub>3</sub> solutions of ketones 1 and 2 are summarized in Table 1 and those of enones 3 and 4 in Table 2.

TABLE 1

$^{19}\text{F}$ - and  $^1\text{H}$  chemical shifts,  $J_{\text{HF}}$  - and  $J_{\text{HH}}$  values of ketones 1 & 2

|                     | <u>1</u>    | <u>2a</u>   | <u>2b</u>  | <u>2c</u> |
|---------------------|-------------|-------------|------------|-----------|
| F                   | -161.9      | -166.7      | -69.5      | -         |
| H(2)                | 4.81 (48.8) | 5.00 (48.0) | 3.21 (8.0) | 2.35      |
| H <sub>ax</sub> (3) | 1.95 (9.8)  | 1.75 (11.0) | 1.70       | 1.68      |
| He <sub>q</sub> (3) | 2.34 (6.0)  | 2.16 (5.2)  | 1.98       | 1.68      |
| He <sub>q</sub> (4) | 1.24 (6.5)  | -           | -          | -         |
| H <sub>ax</sub> (6) | 2.25 (0.0)  | 2.49 (0.0)  | 2.49       | 2.35      |
| He <sub>q</sub> (6) | 2.43 (6.0)  | 2.40 (5.8)  | 2.35       | 2.35      |

$$^2J_{\text{HH}}: \text{H}(3)\text{H}(3) = 12.0 - 13.5; \text{H}(5)\text{H}(5) = 13.2;$$

$$\text{H}(6)\text{H}(6) = 11.8 - 13.9;$$

$$^3J_{\text{HH}}: \text{H}(2)\text{H}_{\text{ax}}(3) = 11.2 - 13.0; \text{H}(2)\text{He}_{\text{q}}(3) = 5.2 - 6.4;$$

$$\text{H}_{\text{ax}}(5)\text{H}_{\text{ax}}(6) = 13.2 - 13.7; \text{H}_{\text{ax}}(5)\text{He}_{\text{q}}(6) = 4.0 - 4.7;$$

$$\text{He}_{\text{q}}(5)\text{H}_{\text{ax}}(6) = 5.5 - 6.8; \text{He}_{\text{q}}(5)\text{He}_{\text{q}}(6) = 2.2 - 3.0;$$

$$^4J_{\text{HH}}: \text{H}(2)\text{H}_{\text{ax}}(6) = 0.1 - 0.8; \text{He}_{\text{q}}(3)\text{He}_{\text{q}}(5) = 2.4 - 3.0.$$

The following aspects are worth being specified:

a) In compounds 1, 2a and 3a the fluorine atom is equatorial; the  $^2J_{\text{HF}}$  values ( $J = 48.0 - 48.2$ ) are slightly smaller than for five membered  $\alpha$ -fluoro ketones ( $J = 51.0 - 51.5$ ) [10,11]. Similarly, the  $^3J_{\text{FH}}$  values for the trifluoromethyl ketones 2b and 3b

TABLE 2

$^{19}\text{F}$ - and  $^1\text{H}$  chemical shifts,  $J_{\text{HF}}$  - and  $J_{\text{HH}}$  values of enones 3 & 4

|                     | <u>3a</u>  | <u>3b</u>  | <u>3c</u> | <u>4a</u>          | <u>4b</u>                |
|---------------------|--|------------|-----------|--------------------|--------------------------|
| F                   | -153.7   | -68.6      | -         | -146.1             | -149.4                   |
| H(2)                | 5.90 (4.4)   | 5.85       | 5.82      | 5.92 (0.8)         | 5.96 (0.8)               |
| H <sub>ax</sub> (5) | 2.10 (9.2)   | 2.01       | 1.90      | 1.92 (32.8)        | 1.83 (36.2)              |
| H <sub>eq</sub> (5) | 2.30 (7.5)   | 2.12       | 1.90      | 2.27 (13.0)        | 2.22 (14.0)              |
| H(6)                | 5.11 (48.0)  | 3.23 (8.4) | 2.45      | -                  | -                        |
| FCH <sub>2</sub> R  | -  | -          | -         | 1.49 (22.4)        | 2.75 (15.0)              |
|                     |  |            |           | R: CH <sub>3</sub> | 2.48 (30.8)              |
|                     |  |            |           |                    | R: C(Me)=CH <sub>2</sub> |
| $^2J_{\text{HH}}$ : | H(5)H(5) = 13.0 - 14.8;  |            |           |                    |                          |
| $^3J_{\text{HH}}$ : | H(2)H(3) = 10.0 - 10.2; H <sub>ax</sub> (5)H(6) = 13.1 - 13.4; |            |           |                    |                          |
|                     | H <sub>eq</sub> (5)H(6) = 5.0 - 5.8;                           |            |           |                    |                          |
| $^4J_{\text{HH}}$ : | H(3)H <sub>eq</sub> (5) = 1.2 - 2.2.                           |            |           |                    |                          |

( $J = 8.0 - 8.4$ ) are again smaller than the corresponding values ( $J = 10.2 - 10.5$ ) in cyclopentanones and cyclopent-2-enones [12,13].

b) In 6-alkyl-6-fluorocyclohex-2-enones the fluorine is axial; this is reflected in the  $^3J_{\text{FH}}$  values ( $J_{\text{F}_{\text{ax}}\text{H}_{\text{ax}}} = 33 - 37$  Hz and  $J_{\text{F}_{\text{ax}}\text{H}_{\text{eq}}} = 13 - 14$  Hz), respectively.

## EXPERIMENTAL

The  $^{19}\text{F}$ -NMR spectra were recorded at 75.4 MHz on a *Bruker WP 80* and the  $^1\text{H}$ -NMR spectra at 400 MHz on a *Bruker WH 400* spectrometer.

Ketones 1 [8,14], 2b & 2c [12] and enones 3b [12], 3c [15] & 4b [16] were synthesized according to published procedures.

Ketone 2a and enones 3a & 3b were synthesized according to [8] from the corresponding silyl enol- or dienol ethers. *4,4-Dimethyl-2-fluorocyclohexanone* (2a, n.c.): 72%, m.p. 71°, MS (m/z) 144 ( $\text{M}^+$ , 31%), 55 (100%). *4,4-Dimethyl-6-fluorocyclohex-2-enone* (3a [17]): 70%. *6-Fluoro-4,4,6-trimethyl-cyclohex-2-enone* (4a, n.c.): 65%, b.p. 72°/0.5 mm, MS (m/z) 156 ( $\text{M}^+$ , 32%), 96 (100%).

## ACKNOWLEDGMENT

The authors are grateful to Dr. T. Umemoto (Sagami Research Center) for a generous gift of N-fluoropyridinium triflate, to Mrs. S. Weidner and Mr. E. Haupt for recording the NMR spectra and to the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

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