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^{13}C NMR AND THEORETICAL CALCULATIONS OF SILYL KETONES AND THIOKETONES

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Abstract. MNDO calculations of $(Me_3C)_2C{=}X$, $(Me_3C)(Me_3Si)C{=}X$, $(Me_3Si)_2C{=}X$, where X=O,S, are reported. It is shown that the large downfield shifts of the carbonyl and thiocarbonyl carbons observed upon silylation correspond to a remarkable increase of negative charge in the same atoms. For acylsilanes a linear correlation between $\delta_{C=O}$ and λ_{max} is found; this indicates that the mean molecular excitation energy component of the paramagnetic shielding contributes significantly to the chemical shift. The unexpectedly low $\delta_{C=S}$ and λ_{max} values reported for bis(trimethylsilyl)thioketone are discussed.

It is known that within a class of structurally related compounds the chemical shift differences of heteroatoms such as nitrogen[1] or sulfur[2] are dominated by the mean molecular excitation energy component of the paramagnetic shielding[3]. It is also known that the same component may significantly affect the chemical shift of the carbons of compounds containing heteroatoms, cf. the series $t\text{-}Bu_2C{=}X$ for which it was shown that the progressive deshielding of the C=X carbon observed when X changes along the 16th column of the periodic table, is paralleled by a progressive increase of the electronegative character of the same atom and that there is a linear correlation between $\delta_{C=X}$ and λ_{max}.[4]

We report here a ^{13}C NMR and theoretical investigation on $(Me_3)_2C{=}X$, $(Me_3C)(Me_3Si)C{=}X$, $(Me_3Si)_2C{=}X$ for X=O,S and discuss some electronic features of these compounds in relation to their ^{13}C NMR spectra.

RESULTS AND DISCUSSION

The synthesis and the physicochemical properties of silyl ketones and thioketones are a matter of current interest[5-8]. Among the unusual spectroscopic features of these compounds[8], there is the downfield ^{13}C NMR resonance of the quaternary C=X (X=O,S) carbon, which is often taken as a criterion for structural assignments[5a,b]. Thus, a correct interpretation of the factors at the origin of $\delta_{C=X}$ is a necessary requirement to assign the chemical shifts to new systems.

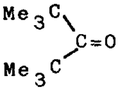
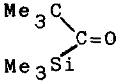
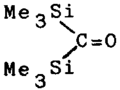
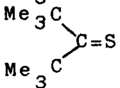
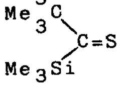
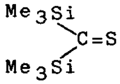
Table 1 gives the $\delta_{C=X}$ and λ_{max} values and the MNDO total charges, q_C and q_X of bis(trimethylsilyl), (t-butyl)(trimethylsilyl) and di-t-butyl ketones (1-3) and thioketones (4-6).

Table 1 shows that silylation of ketones leads to a progressive increase of the electronic charge in the carbonyl carbon and that, in agreement with previous assumptions[9], most of the variation in atomic charge arises from σ electrons. The great electronegative character of the carbonyl carbon of bis(trimethylsilyl)ketone is in agreement with preliminary reactivity tests[5c] showing it to be a synthetic equivalent for dianion CO^{2-}.

Based on the charge/shift correlations observed by Flizsàr et al.[14] for dialkyl ketones, it has been suggested that the chemical shifts of silyl ketones are sufficiently accounted for in terms of carbonyl carbon's atomic charge variations[9]. However, Table 1 shows that on going from 1 to 2 the replacement of a t-butyl group by $SiMe_3$ increases λ_{max} by 69 nm and deshields the carbonyl carbon by 31 ppm. Further replacement of the t-butyl group by $SiMe_3$ on going from 2 to 3 increases λ_{max} by 173 nm and deshields the carbonyl carbon by 69 ppm. In other words there is a linear correlation between $\delta_{C=0}$ and λ_{max} ($\delta_{C=0} = 96.512 + 0.411\, \lambda_{max}$; r=0.999). This indicates that $\delta_{C=0}$ depends not only on the atomic charge but also on the average excitation energy component of the paramagnetic shielding[3]. Indeed the increase of λ_{max} on going from 1 to 3 arises from the decrease of $n \rightarrow \pi^*$ or $\sigma \rightarrow \pi^*$ excitation energies[8a] and it is also known that, contrary to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or $\sigma \rightarrow \pi^*$ transitions are the major contributions to ΔE[3]. Thus, by analogy with $t\text{-}Bu_2C=X$ (X=O, S, Se) derivatives[3], most of the increase in $\delta_{C=0}$ observed by passing from 1 to 3 is likely to arise from the effect of the decrease of ΔE which counteracts and overwhelms the effect of the increase of negative charge.

Table 1 shows that the variation of the total charge of carbon for thioketones 4-6 follows the same trend as that of ketones 1-3. Silylation again leads to the progressive increase of σ charge in carbon. An inversion in the polarization of the C=S bond is observed even in the monosilyl thioketone, which in this respect is more similar to the disilyl than to the monosilyl ketone. We have found that the HOMO and the LUMO MO's of 1-3 and 4-6 have n_X and $\pi^*_{C=X}$ character with the HOMO-LUMO energy differences decreasing progressively with silylation (11.42, 10.55 and 9.60

Table 1. Carbon-13 chemical shifts[a] ($\delta_{C=X}$, X=O,S), and total charges[b] of compounds 1-6

Compound		$\delta_{C=X}$,ppm	λ_{max} ,nm	q_C,me-	q_X,me-	q_C,me-
1.	 $(Me_3C)_2C=O$	218.0[c,d]	298[d]	+ 237	- 307	+ 276
2.	 $(Me_3C)(Me_3Si)C=O$	249.0[c]	367[e]	- 45	- 299	+ 258
3.	 $(Me_3Si)_2C=O$	318.2[c]	540[f]	- 335	- 272	+ 229
4.	 $(Me_3C)_2C=S$	278.0[d]	540[d]	- 99	- 25	+ 152
5.	 $(Me_3C)(Me_3Si)C=S$	316.0	606	- 429	+ 5	+ 120
6.	 $(Me_3Si)_2C=S$	267[g] (402)[h]	530[g] (756)[h]	- 793	+ 64	+ 73

(a) In CHCl3, from TMS; (b) MNDO, fully optimized geometry; (c) From ref.9
(d) From ref. 4 ; (e) From ref. 10 ; (f) From ref. 5c,b; (g) From ref. 11;
(h) Predicted values (see text)

eV for 1, 2, 3 and 8.47, 8.29, 7.99 for 4, 5, 6). For the monosilylderivatives our data is in agreement with already published ab initio calculations[15,16].

Since it is known that the transformation of ketones into the corresponding thioketones leads invariably to the red shift of the maximum UV absorption[12], an increase of λ_{max} on going from ketones 1-3 to thioketones 4-6 is expected. Moreover the increase of λ_{max} passing from ketones to the corresponding thioketones is invariably accompanied by a downfield shift in unsaturated carbon amounting to several ppm[5a]. For different classes of ketones and thioketones there is a linear relationship between the chemical shifts of C=O and C=S carbons, which enables one to predict the chemical shifts of the thioketones from the corresponding ketones within a few ppm[13]. The general validity of such $\delta_{C=S}$ vs. $\delta_{C=O}$ correlations has recently been confirmed[13c]. Therefore a progressive increase of $\delta_{C=S}$ on going from 4 to 6 is expected.

Table 1 shows that the replacement of a t-butyl group by $SiMe_3$ on going from 4 to 5 increases λ_{max} by 66 nm and deshields the unsaturated carbon by 38 ppm, in agreement with what is observed in several monosilylthioketones[5a]. However, contrary to expectations, the chemical shift and the λ_{max} reported for 6 are much smaller than those of the mono silylated derivative and of the corresponding ketone 3. This is surprising since according to our MNDO calculations the electronic structure of 6 is in the same relation with that of 4 and 5 as is 3 with 1 and 2. On the basis of the relationship $\delta_{C=S} = 10.77 + 1.23\ \delta_{C=O}$, derived from 1,2 and 4,5, a chemical shift of 402 ppm would be expected for 6. For such $\delta_{C=S}$ value and assuming a linear relationship between $\delta_{C=S}$ and λ_{max}, a λ_{max} of 756 nm for 6 is also calculated.

The fact that both $\delta_{C=S}$ and λ_{max} reported for bis(silyltrimethyl)thioketone are much lower than the values derived from empirical correlations and that nothing in the MNDO electronic structure of this compound justifies such anomalous behaviour, indicates that either the values reported for 6 do not correspond to the proposed structure or that this compound is a very special thioketone whose electronic configuration requires a much deeper theoretical treatment. The problem is relevant in relation to the potential synthetic utility of this compound[6].

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