Tetrahedron Vol. 42, No. 13, pp. 3607 to 3610, 1986
Printed in Great Britain.

0040-4020/86 \$3.00 + .00
Pergamon Journals Ltd.

A C-13 NMR AND THEORETICAL STUDY OF THE ELECTRONIC STRUCTURE OF ACYLSILANES

F. BERNARDI,[a] L. LUNAZZI,[a] A. RICCI,[b]
G. SECONI,[c] and G. TONACHINI[a]

a) Istituto di Chimica Organica - Università -
V.le Risorgimento 4, Bologna (Italy)

b) Dipartimento di Chimica Organica e Centro CNR sulla Chimica
e Struttura dei Composti Eterociclici e loro Applicazioni.
Via G. Capponi, 9 - Firenze (Italy)

c) Istituto CNR dei Composti del Carbonio Contenenti Eteroatomi
e loro Applicazioni. Ozzano Emilia, Bologna (Italy)

(*Received in UK* 20 *January* 1986)

Abstract - The results of a C-13 NMR study on a series of acylsilanes and carbon analogs are reported. The results are rationalized in terms of a theoretical analysis based on the σ and π charge components of XH_3 and HC=O moieties.

INTRODUCTION

During the last few years there has been a continuous and considerable interest in the synthesis,[1] reactivity,[2] and synthetic applications[3] of acylsilanes. All the spectroscopic features point out the inadequacy of this class of compounds to be represented by classical ketonic structures; however theoretical investigations have not been so far performed in order to obtain a detailed insight into the still unsolved problem of the actual electronic structure of acylsilanes. To obtain additional information about the electronic structure of these compounds we have performed a C-13 NMR study of a series of acylsilanes and carbon analogs coupled with a theoretical analysis of the extent and direction of the σ and π charge components of XH_3 and HC=O moieties. In this paper we report the results of such a study.

RESULTS AND DISCUSSION

We have observed that the C-13 signals of the carbonyl groups in acylsilanes (R_3Si-CO-R') are dramatically shifted downfield with respect to those of the corresponding ketones (R_3C-CO-R'): the values reported in the Table for few selected derivatives indicate that the carbonyls in acylsilanes have chemical shifts differing by 25 up to 103 ppm from those of the analogous ketones (derivatives **3,9** and **4,7** respectively in the Table). This fact is surprising in that substitution by silylated groups is expected to move upfield the C-13 signals of a directly bonded carbon (α-carbon). Indeed we checked (see Table) that sp^2 carbons other than carbonyl (e.g. ethylenic and aromatic) are shifted upfield rather than downfield when an α-alkyl is replaced by an α-silyl group (see derivatives **5**,**10** and **6**,**11** in the Table). These results might be interpreted in terms of the inverse effect of σ and π charges. It has already been pointed out[5] that an increase in total electron population at carbon is accompanied

(i) by a high-field shift when the electron enrichment results from a gain in π charge prevailing over the concurrent loss in σ electrons (a situation encountered with aromatic and vinyl carbon and carbonyl oxygen atoms) or

(ii) by a downfield shift when the increase in charge is dictated by that of the σ population (a situation encountered with sp^3 carbon, carbonyl carbon and dialkyl ether oxygen atoms).

On the basis of these trends it follows that the silyl group in acylsilanes should act mainly as a σ donor. To confirm this hypothesis we have performed ab-initio SCF-MO computations[6] at STO-3G* level[7a] on the simple species $H_3Si\text{-}HC{=}O$ and, for the sake of comparison, also on $H_3C\text{-}HC{=}O$. The computations in the latter case have been performed at the STO-3G level[7b] with the inclusion of a set of d orbitals on the methyl carbon. First a full geometry optimisation of the staggered and eclipsed conformers was performed and it was found that in both cases the minimum of the torsional potential corresponds to the eclipsed geometry. Details of the geometrical parameters will be given elsewhere.[8] The interest of the present work mainly focuses on the analysis of the effect of these substituents. The pertinent informations are summarized in the Scheme below where the total charge of the groups H↘C=O, SiH_3[9] and CH_3, together with the σ and π components have been reported.

The total charges of the fragments have been estimated in terms of the results of the population analysis while the σ and π components have been computed on the basis of a quantitative orbital analysis.[10] To this purpose, the molecule has been decomposed into the H_3X- and HC=O fragments.

The comparison shows the following points:

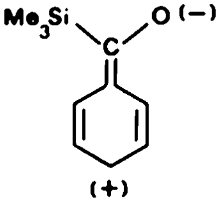
(i) both CH_3 and SiH_3 act, with respect to a carbonyl group, as electron donors. However, while the overall electron transfer associated with the SiH_3 group is significant (~ 0.2e), that associated with the CH_3 group is negligible (~ 0.02e).

(ii) the SiH_3 group acts as a σ donor and a π acceptor, with the σ effect being larger and dominant.

(iii) in the CH_3 group both effects operate in the same direction and are much smaller.

(iv) in both cases we have decomposed the π effect into the contribution associated with the π-type orbitals of the XH_3 groups and that associated with d_π -type orbitals of the X atoms. We have found that in both cases these groups act as π_{XH_3} donors and d_π acceptors: for SiH_3 the magnitude of the two contributions are 0.077e and 0.098e respectively, so that the dominant effect is that associated with the d_π orbitals, while for CH_3 the two quantities become 0.025 and 0.012 and the dominant effect is that associated with the π_{CH_3} orbitals.

The experimental results of the Table show also a second feature that is worth mentioning. Whereas the carbonyl of an alkyl phenyl ketone (e.g. Ph-CO-tBu) has a shift close to its aliphatic analog (e.g. Me-CO-tBu), the difference between the two corresponding silylated derivatives ($Ph-CO-SiMe_3$ and $CH_3-CO-SiMe_3$), is quite large in that the CO of the benzoyltrimethylsilane **3** is 14 ppm upfield with respect to acetyltrimethylsilane **2**. This effect might be attributed to the contribution of resonance structures like



that reduce the amount of the positive charge on the carbonyl carbon, thus increasing its shielding and displacing, consequently, the chemical shift upfield with respect to the case of the aliphatic derivative **2** ($CH_3-CO-SiMe_3$) where such a resonance contribution obviously does not operate. Apparently this effect does not occur in the phenylpivaloylketone **9** (Ph-CO-tBu) since the bulky t-butyl group twists the phenyl ring out of the plane of the carbonyl, thus making the conjugation much less efficient. As a consequence the carbonyl of **9** has a shift almost equal to that of its aliphatic analog **8**. This behaviour can be understood on the basis of the C-Si (1.85 Å) that is larger than the C-C (1.50 Å) bond; this makes less difficult for the phenyl ring to adopt the planar arrangement required for the conjugation.

EXPERIMENTAL

Spectra were recorded at 75.46 MHz with a Bruker CXP 300 spectrometer (High field NMR service of the CNR) in the FT mode with proton decoupling. Identification of the quaternary sp^2 carbon was easily performed on the basis of their much longer relaxation time. In the case of $CH_2=CH-X$, off-resonance experiments allowed to assign the signals of CH (a doublet) and CH_2 (a triplet).

Compounds **5-11**, were commercially available and were purified before running the NMR spectra. Previously reported procedures were employed for the synthesis of **1**,**2** (ref 1b), **3** (ref 1a), and **4** (ref 13).

Table. ^{13}C-NMR chemical shifts in $CDCl_3$ (ppm **from TMS**) **for** some sp^2 carbons directly bonded to $SiMe_3$ and to CMe_3. The difference (Δ) of the shifts of column 1 and 2 are positive for 1-4 but negative for the ethylenic and aromatic derivatives (5,6).

Compound	X= $SiMe_3$	X= CMe_3	Δ
Me_3C-CO-X	**1** 249.0	**7** 215.1	33.9
CH_3-CO-X	**2** 247.6^{a}	**8** 210.4	37.2
Ph-CO-X	**3** 233.6^{b}	**9** 209.1^{c}	24.5
Me_3Si-CO-X	**4** 318.2	**1** 249.0	69.2
CH_2=CH-X	**5** 140.2	**10** 148.1	-7.9
Ph-X	**6** 142.2	**11** 150.1	-8.0

[a] Lit. 248.7, ref 11. [b] Lit. 236.7, ref 11. [c] Lit. 206. ref. 12; 209.2, ref 11.

REFERENCES

1. a) A.G. Brook, Adv.Organomet.Chem., **1968**, 7, 95; b) E.J. Corey, D. Seebach, and R. Freedman, J.Am.Chem.Soc., **1967**, 89, 434; c) A. Degl'Innocenti, D.R.M. Walton, G. Seconi, G. Pirazzini, A. Ricci. Tetrahedron Lett., **1980**, 3927; d) H. Reich, and M. Kelly, J.Am.Chem.Soc., **1982**, 104, 1119; e) K. Yamamoto, S. Suzuki, J. Tsuji, Tetrahedron Lett., **1980**, 1653.
2. A.G. Brook, Acc.Chem.Res., **1974**, 7, 77; A. Wright, and R. West, J.Am.Chem.Soc. **1974**, 96, 3214; A.G. Brook, and R. Bassindale, "Rearrangements in Ground and Excited States" (Edited by P. de Mayo), Vol. 2 pp 149-221, Academic Press, New York (1980); D. Pietropaolo, M. Fiorenza, A. Ricci, M. Taddei, J.Organomet.Chem., **1980**, 197, 7.
3. A. Degl'Innocenti, S. Pike, D.R.M. Walton, G. Seconi, A. Ricci, and M. Fiorenza, J.Chem.Soc., Chem.Commun., **1980**, 1201; H. Reich, M. Kelly, R.E. Olson, and C.R. Holtan, Tetrahedron, **1983**, 39, 949, and references therein; A. Ricci, A. Degl'Innocenti, S. Chimichi, M. Fiorenza, G. Rossini, and H.J. Bestmann, J.Org.Chem., **1985**, 50, 129.
4. J.B. Stothers, "Carbon-13 NMR Spectroscopy". Chp 5, p. 158, Academic Press, New York, 1972.
5. S. Fliszar, G. Cardinal, and M.T. Beraldin, J.Am.Chem.Soc., **1982**, 104, 5287.
6. J.S. Binkely, R.A. Whiteside, R. Krishnan, R. Seeger, D.J. De Frees, H.B. Schlegel, S. Topiol, L.R. Kahn, and J.A. Pople, Gaussian 80,QCPE, **1981**, 13, 406
7. a) J.B. Collins, P. v.Schleyer, J.S. Binkley, and J.A. Pople, J.Chem.Phys., **1976**, 64, 5142; b) W.J. Hehre, R.F. Stewart and J.A. Pople, J.Chem.Phys., **1969**, 51, 2657.
8. F. Bernardi, A. Ricci, and G. Tonachini, in preparation.
9. A similar total charge distribution in the H_3Si-HC=O molecule has been recently calculated in the course of a theoretical investigation on methylsilenone and its isomers: M.S. Gordon, and C. George, J.Am.Chem.Soc., **1984**, 106, 609.
10. F. Bernardi, and A. Bottoni, Theor.Chim.Acta, **1981**, 58, 245; F. Bernardi, and A. Bottoni, in R. Daudel and I.G. Csizmadia, "Computational Theoretical Organic Chemistry", Reidel 1981.
11. E.M. Dexheimer, G.L. Buell, and C. Le Croix, Spectrosc.Lett., **1978**, 11, 751.
12. K.S. Dhami, and J.B. Stothers, Can.J.Chem., **1965**, 43, 479.
13. A. Ricci, M. Fiorenza, A. Degl'Innocenti, G. Seconi, P. Dembech, K. Witzgall, and H.J. Bestmann, Angew.Chem., Int. Ed., **1985**, 24, 1068.