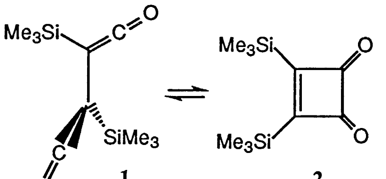
^{13}C, ^{17}O, and ^{29}Si NMR Spectra and Stabilization of Silylated Ketenes and Bisketenes

Annette D. Allen, Ian Egle, Rudolf Janoschek,[†] Hui Wen Liu, Jihai Ma, Romeo M. Marra, and Thomas T. Tidwell*
Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1
[†]*Institut für Theoretische Chemie, Karl-Franzens Universität, A-8010 Graz, Austria*

(Received September 4, 1995)

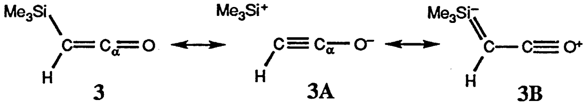
The experimental and calculated ^{13}C, ^{17}O, and ^{29}Si NMR chemical shifts of silylated ketenes and bisketenes show trends consistent with charge redistribution resulting from neutral hyperconjugative donation from the R_3Si-C bond to the p orbital on the carbonyl carbon, and are supportive of this mechanism for the striking stability of these species.

The remarkable stability of silylketenes has been utilized in our laboratory for the preparation of bisketenes **1**, which are thermodynamically stable towards ring closure to cyclobutenediones **2**.[1]



1 **2**

There is disagreement about the origin of the stabilizing influence of silyl substituents on ketenes. It was suggested by Brady and Cheng[2] that this effect arose from hyperconjugative donation from the C–Si bond into the in-plane carbon p orbital of the carbonyl group, as represented by the resonance structure **3A**.[2] This proposal was disputed by Runge, who instead argued that the silicon acted as a d_π–p_π electron acceptor, as represented by **3B**.[3] These two mechanisms give opposite predictions of the direction of electron redistribution in ketenes due to silyl group substitution.

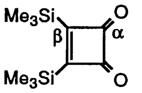
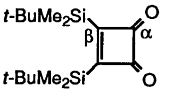


3 **3A** **3B**

Our previous studies using *ab initio* molecular orbital calculations of the geometries and energies of silylketenes, are not definitive as to the origin of the stabilization of these compounds.[4] This effect is related to the stabilization of β-silyl carbocations and radicals[5], and the interaction shown in **3A** is an example of "neutral hyperconjugation", as recently discussed by Lambert and Singer.[5]

Nuclear magnetic resonance spectroscopy is a powerful tool for the examination of electronic distributions in molecules, but ^{13}C and ^{17}O NMR have been utilized in only a few applications in ketenes,[6] while ^{29}Si NMR[7] has not previously been applied to ketenes. We now report an examination of NMR chemical shifts of silylketenes, studying multiple nuclei and structurally analogous substrates to guard against ambiguities in the interpretation.

Table 1. NMR Chemical shifts in $CDCl_3$ of ketenes and reference compounds (this work unless noted)

Ketene	δ ^{13}C (C_α)	δ ^{17}O	δ ^{29}Si
$Me_2C{=}C{=}O$	204.9[a]	329[a]	
t-$Bu_2C{=}C{=}O$	203.4	330.6 (331.5)[b]	
$PhCMe{=}C{=}O$	205.6[a]		
$Ph_2C{=}C{=}O$	201.3[a]	340[a,b]	
$Me_3SiCH{=}C{=}O$	179.2[a]	255.0	–0.2
$Me_3SiCPh{=}C{=}O$	182.5		–0.6
$(Me_3SiC{=}C{=}O)_2$	181.8	269.2 (269.0)[b]	3.2
$(t$-$BuMe_2SiC{=}C{=}O)_2$	182.2	270.5	10.6
$Me_3SiCH_2CO_2H$			3.8
$Me_3SiCH_2CO_2Et$			3.2[c]
$Me_3SiCH_2COCH_3$	206.8	536.7	1.6
	202.0	499.1	–8.4
	202.1		0.4
CH_3COCH_3	206.5	565.3 (571)[b,d]	
$Me_3SiCH{=}CH_2$			–6.6[c]
$Me_3SiC_6H_5$			–4.5[c]
t-$BuMe_2SiCH{=}CH_2$			0.9

[a]Ref. 6 [b]CH_3CN solvent [c]Ref. 7 [d]Ref. 9

In Table 1 are collected ^{13}C, ^{17}O, and ^{29}Si chemical shifts measured[8] in this laboratory in $CDCl_3$ solution for ketenes and other reference compounds, together with selected literature data. To ensure that the ^{17}O shifts were not affected by hydrogen bonding[9] with $CDCl_3$ several compounds were also measured in CH_3CN solutions, and as noted in the Table the solvent effects are small.

The ^{13}C shifts of the carbonyl carbons (C_α) of $Me_2C{=}C{=}O$, $PhCMe{=}C{=}O$, and $Ph_2C{=}C{=}O$ fall in the range δ 201.3 to 205.6. By contrast in the Me_3Si substituted ketenes and bisketenes C_α appears from δ 179.2 to 182.5, showing an upfield shift of 18.8 to 26.4 ppm due to Me_3Si substitution on ketenes. The ^{17}O shifts are even more dramatic, with the non-silylated ketenes absorbing from δ 329 to 340, while the silylated ketenes and bisketenes absorb from 255 to 270 ppm, giving upfield shifts upon silyl substitution of 59 to 85 ppm. Thus both the ^{13}C and ^{17}O shifts of the carbonyl group in ketenes and bisketenes are shifted strongly upfield relative to the nonsilylated models, consistent with major electron donation from the Me_3Si-C bond in ketenes, as represented by **3A**. By contrast substitution at C_β for either methyl or hydrogen by phenyl groups, which interact with the alkenyl moiety by normal p_π-p_π conjugation, shows no significant effects on the $^{13}C_\alpha$ or ^{17}O shifts (*cf* the values for δ $^{13}C_\alpha$ of 204.9, 205.6, and 201.3 for $Me_2C{=}C{=}O$, $PhCMe{=}C{=}O$, and $Ph_2C{=}C{=}O$, respectively, and those of 179.2 and 182.5 for $Me_3SiCH{=}C{=}O$ and $Me_3SiCPh{=}C{=}O$, respectively).

By contrast the ^{29}Si chemical shifts for Me_3Si groups bonded to sp^2 carbon in $Me_3SiCH{=}CH_2$, $Me_3SiC_6H_5$ and the cyclobutenedione **2** are δ -6.6, -4.5, and -8.4, respectively, while in the ketenes and bisketenes these are at -0.6 to 3.2, or shifted downfield by 3.9 to 11.6 ppm. These results are thus also consistent with electron withdrawal from the Me_3Si-C bond by the neutral hyperconjugation type of interaction shown in **3A**. All the ^{13}C, ^{17}O, and ^{29}Si results for ketenes are opposite to those expected for the d_π-p_π interaction in **3B**.

Calculation of the chemical shifts by the IGLO method,[10] basis set II, using MP2/6-31G* optimized geometries gave the following results (experimental values in parentheses) for $Me_{\gamma 3}SiC_\beta H{=}C_\alpha{=}O$: Si -6.0 (-0.2); O 275.0 (255.0); C_α 175.4 (179.2); C_β -16.9 (-0.1); H_β 1.45 (1.65); C_γ -7.6, -4.2, -4.2 (0.9); H_γ -0.30 (0.12), for $Me_2C{=}C{=}O$: O 353.7 (329); C_α 215.0 (204.9); C_β 26.9 (24.2); C_γ 9.6 (10.1)[11]; H_γ 0.90, 1.03 (1.58), and for $Me_3SiCH{=}CH_2$ Si -8.9 (-6.6). Thus the calculated values reproduce the large effects of Si substitution on $^{13}C_\alpha$ ($\Delta\delta$ calc 39.6, obs 25.7 ppm), and ^{17}O ($\Delta\delta$ calc 78.7, obs 74 ppm), and the difference in ^{29}Si shift between $Me_3SiCH{=}C{=}O$ and $Me_3SiCH{=}CH_2$ ($\Delta\delta$ calc 2.9, obs 6.4).

The measurement of chemical shifts is also relevant to the elucidation of the interaction of β-silyl groups with electron deficient p orbitals in compounds such as ketones and esters, and in carbocations.[5] There are downfield ^{29}Si shifts for Me_3SiCH_2COR (R = Me, OH, OEt) of 1.6 to 3.8 ppm relative to Me_4Si, consistent with hyperconjugative electron donation analogous to that shown in **3A**. However β-Me_3Si substituents apparently do not cause any noticeable effect on the carbonyl ^{13}C shifts of ketones, as exemplified in the shift for acetone (Table).

The effect on the ^{17}O chemical shift of acetone by substitution of Me_3Si is also quite substantial, causing a shift of 28.6 ppm upfield for $Me_3SiCH_2COCH_3$ compared to CH_3COCH_3. By contrast the β-*tert*-butyl group causes a downfield shift of 6 ppm for *t*-$BuCH_2COCH_3$ compared to CH_3COCH_3.[9] A comparison of the effect of Me_3Si substitution on ketenes and ketones is available from the ratio 2.6 of the ^{17}O shift of 74 ppm upfield of $Me_3SiCH{=}C{=}O$ compared to $Me_2C{=}C{=}O$ and 28.6 ppm upfield of $Me_3SiCH_2COCH_3$ compared to CH_3COCH_3. For the ^{29}Si shifts the comparable ratio is 4.0 of the 6.4 ppm downfield shift of $Me_3SiCH{=}C{=}O$ compared to $Me_3SiCH{=}CH_2$, and 1.6 ppm downfield of $Me_3SiCH_2COCH_3$ compared to Me_4Si. Thus the effect of β-Me_3Si substitution on the ^{17}O and ^{29}Si chemical shifts in ketenes and ketones is roughly proportional, and is consistent with neutral hyperconjugation as shown in **3A**.

In conclusion the ^{13}C, ^{17}O, and ^{29}Si NMR chemical shifts of silyl-substituted ketenes and bisketenes are all consistent with decreased negative charge on silicon, and increased negative charge on the carbonyl carbon and oxygen, when compared to model non-silylated ketenes, or to silylated alkenes. The charge distribution is highly supportive of an important role for the "neutral hyperconjugation" interaction shown in **3A**. Calculated chemical shifts reproduce the effects of silyl substitution found experimentally. There is further evidence for this interaction from the ^{17}O and ^{29}Si shifts of β-trialkylsilyl ketones, esters, and acids.

Grateful acknowledgement is made to Nick Plavac for the ^{17}O and ^{29}Si NMR measurements, Professors Zvi Rappoport and Giovanni Ceroni for helpful discussions, and to the Natural Science and Engineering Research Council for financial support.

References and Notes

1 T. T. Tidwell, *Ketenes*, Wiley, New York (1995), Chap. 4.5; D.-c. Zhao, A.D. Allen, and T. T. Tidwell, *J. Am. Chem. Soc.*, **115**, 10097 (1993); M. A. McAllister and T. T. Tidwell, *J. Am. Chem. Soc.*, **116**, 7233 (1994); A. D. Allen, J. Ma, M. A. McAllister, T. T. Tidwell, and D.-c. Zhao, *Acc. Chem. Res.*, **28**, 265 (1995).

2 W. T. Brady and T. C. Cheng, *J. Org. Chem.*, **42**, 732 (1977).

3 W. Runge, *Prog. Phys. Org. Chem.*, **13**, 315 (1981).

4 A. D. Allen and T. T. Tidwell, *Tetrahedron Lett.*, **32**, 847 (1991); L. Gong, M. A. McAllister, and T. T. Tidwell, *J. Am. Chem. Soc.*, **113**, 6021 (1991).

5 J. M. White, *Aust. J. Chem.*, **48**, 1227 (1995); J. B. Lambert, *Tetrahedron*, **46**, 2677 (1990); J. R. Hwu, B.-L. Chen, L. W. Huang, and T.-H. Yang, *J. Chem. Soc., Chem. Commun.*, **1995**, 299; J. B. Lambert and R. A. Singer, *J. Am. Chem. Soc.*, **114**, 10246 (1992).

6 J. Firl and W. Runge, *Z. Naturforsch*, **29B**, 393 (1974); H. Duddeck and H.-W. Praas, *Magn. Reson. Chem.*, **31**, 182 (1993); Yu. K. Grishin, S. V. Ponomarev, and S. A. Lebedev, *Zh. Org. Khim.*, **10**, 404 (1974). G. Cerioni, A. Plumitallo, J. Frey, and Z. Rappoport, *Magn. Reson. Chem.*, **33**, 669 (1995).

7 H. Marsmann, In *NMR Basic Principles and Progress*, Vol. 17, P. Diehl, E. Fluck, and R. Kosfeld, Eds., Springer-Verlag, Berlin (1981); E. A. Williams, In *The Chemistry of Organic Silicon Compounds*, Chap. 8, S. Patai and Z. Rappoport, Eds., Wiley, New York (1989); H. Sakurai, Y. Kamiyama, A. Mikoda, T. Kobayashi, K. Sasaki, and Y. Nakadaira, *J. Organomet. Chem.*, **201**, C14-C18 (1980).

8 The ^{17}O and ^{29}Si NMR spectra were measured in 5 mm tubes at a temperature of 20.5±0.5 °C with a Varian VXR 400S instrument operating at 54.219 MHz for ^{17}O and 79.459 MHz for ^{29}Si. Concentrations were *ca* 30% v/v for ^{17}O, which are referred to external D_2O ($\delta = 0$) and 5% v/v for ^{29}Si. The ^{29}Si spectra were measured via the DEPT sequence using a value of $^2J_{Si\text{-}H} = 6.7$ Hz and using TMS ($\delta = 0$) as reference.

9 *^{17}O NMR Spectroscopy in Organic Chemistry*, ed by D. W. Boykin, CRC Press, Boca Raton (1991); C. Delseth and J. P. Kintzinger, *Helv. Chem. Acta*, **59**, 466, 1411 (1976).

10 W. Kutzelnigg, U. Fleischer, and M. Schindler, In *NMR - Basic Principles and Progress*, Vol. 23, Springer-Verlag, Berlin (1991). For $Me_3SiCH{=}C{=}O$ the basis set for the Me groups was DZ + POL.

11 Calculated using basis set DZ for Me, experimental Me of $Et(Me)C{=}C{=}O$, Ref. 6.