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# 4,4-DIMETHYLSILACYCLOHEXADIEN-1-ONE

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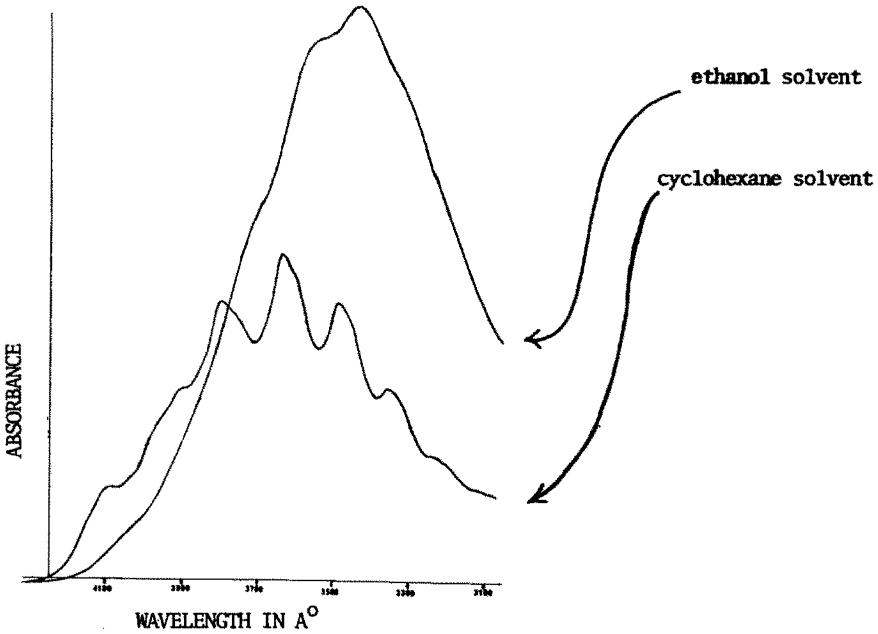
The profound effect of an α-trimethylsilyl group on the n-π* transition of a carbonyl functionality observed by A. G. Brook stimulated our interest in the interactions of silyl centers with the excited states of π-systems.[1,2] While the ultraviolet spectra of numerous α,β-unsaturated carbonyl systems have been reported and the position of their n-π* maxima correlated with the effect of substituents, no system containing a silyl center interacting with a carbonyl functionality through a conjugating carbon-carbon double bond has yet been reported. Such a system is of theoretical interest. Zimmerman has calculated that in the n-π* state of an α,β-unsaturated ketone a charge separation develops in which the β-carbon becomes partially negatively charged while the carbonyl oxygen becomes partially positively charged $\mathrm{C{=}C{-}C{=}O} \xrightarrow{h\nu} {}^{-\delta}\mathrm{C{-}C{=}C{-}O}^{+\delta}$.[3] The fact that silicon has a definite ability to stabilize a negative charge adjacent to it by dπ-pπ overlap as shown by the facile metallation of tetramethylsilane with n-butyllithium[3,4] caused us to suspect that a β-silyl center should have a very pronounced effect on the n-π* transition in an α,β-unsaturated ketone. Certainly, the silyl center should stabilize the developing negative charge adjacent to it in the excited state. For these reasons, we were interested in preparing the title compound--4,4-dimethylsilacyclohexadien-1-one--and in its spectral properties.

4,4-Dimethylsilacyclohexadien-1-one was prepared by the selenium dioxide oxidation of 4,4-dimethylsilacyclohexan-1-one[5] in refluxing t-butanol for 18 hours.[6] The solution was decanted from the precipitated selenium metal, t-butanol distilled off, and the residue chromatographed on silica gel using n-hexane as eluant. This material was then bulb to bulb distilled to separate it from any non-volatile material. The final purification was by preparative gas chromatography on a 12' x 1/4" SE-30 column at 120°C. The overall yield obtained was close to 55%. The nmr is characterized by a singlet at 0.12 δ(6H), and an $A_2B_2$ quartet $\delta_A$ at 6.71 (2H) and $\delta_B$ at 6.98 (2H), $J_{AB}$ = 15 Hz. The nmr was run on a Varian

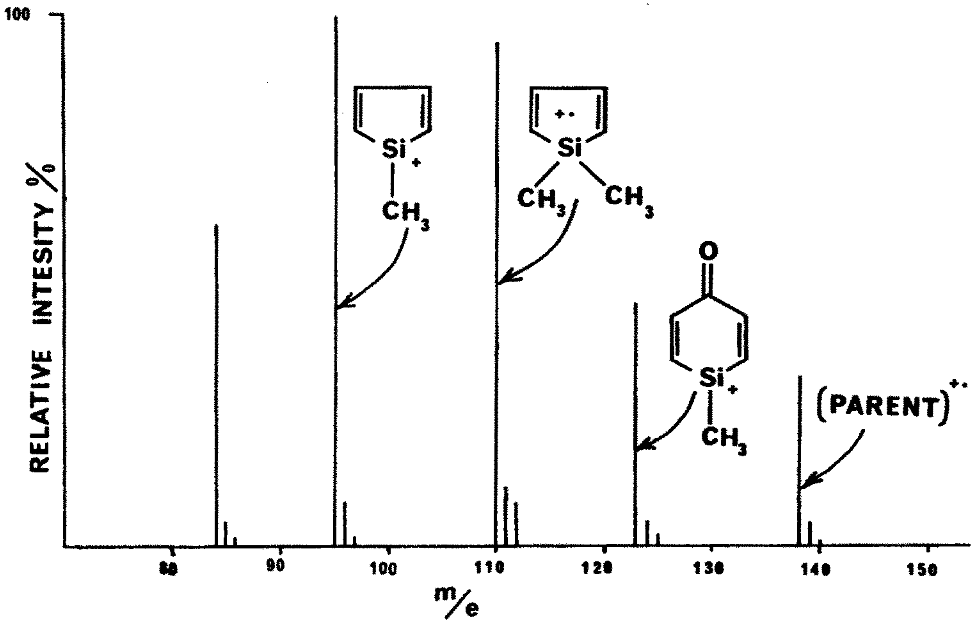
HA-100 instrument using methylene chloride as internal standard. The ir spectrum is characterized by a carbonyl stretch at 1635 $cm^{-1}$ and a carbon-carbon double bond stretch at 1580 $cm^{-1}$. By comparison the carbonyl stretch of acetyltrimethylsilane comes at 1645 $cm^{-1}$.[1] The carbonyl stretch of a normal α,β-unsaturated ketone comes between 1685 - 1665 $cm^{-1}$.[7] The high resolution mass spectrum of 4,4-dimethylsilacyclohexadien-1-one was run on an A.E.I. MS-902. In addition to the parent ion at m/e = 138, a siliconium ion formed by loss of a methyl group from the quarternary silyl center at m/e = 123 is prominent. The parent ion also decomposes by loss of CO to form an ion at m/e = 110. The observation of a metastable ion at m/e = 87.7 (calculated m/e = $(110)^2/138$ = 87.7) supports this pathway. A possible structure for this ion is the dimethylsilacyclopentadienyl cation radical. Loss of a methyl radical from this ion m/e = 110 leads to formation of an ion at m/e = 95. The observation of a metastable ion at m/e = 82 (calculated m/e = $(95)^2/110$) supports this pathway for formation of this ion. A possible structure for this ion m/e = 95 is the methylsilacyclopentadienyl cation.

Of greatest interest is the ultraviolet spectrum of the compound. The n-π* absorption band is characterized by the usual vibrational fine structure. The 0-0 band is found at 4160 Å in cyclohexane. By comparison the 0-0 band in 4,4-dimethylcyclohexadienone occurs at 3770 Å in cyclohexane.[3] This shift to longer wavelength corresponds to a stabilization of the n-π* excited state by the silyl center of 7 kcal. This certainly is in agreement with the effect predicted from Zimmerman's calculations.[3] The most intense vibrational band is the 0-3 band at 3730 Å with an extinction coefficient of 17. The n-π* transition loses considerable vibrational fine structure when ethanol is used as solvent. The center of the now broad absorption (3440 Å) is shifted to shorter wavelength as is usually observed for n-π* transitions in going to polar solvent. A significant increase in the extinction coefficient is observed in ethanol solvent ($\epsilon$ = 30). The π-π* transition for 4,4-dimethylsilacyclohexadien-1-one occurs at 2300 Å with an extinction coefficient of 12,000. This compares with a π-π* transition maximum in 4,4-dimethylcyclohexadienone at 2250 Å. Certainly the silyl center has less effect on the π-π* transition than it does on the n-π* transition.

Absorption Spectra of 4,4-dimethylsilacyclohexadien-1-one n→$\pi^*$ Transition



Mass Spectrum of 4,4-dimethylsilacyclohexadien-1-one



## Acknowledgements

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## References

1. A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, J. Amer. Chem. Soc., 89, 431 (1967).
2. A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, J. Amer. Chem. Soc., 82, 5102 (1960).
3. H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, J. Amer. Chem. Soc., 89, 6589 (1967).
4. D. J. Peterson, J. Organomet. Chem., 9, 373 (1967).
5. R. A. Benkeser and E. W. Bennett, J. Amer. Chem. Soc., 80, 5414 (1958).
6. S. Bernstein, and R. Litell, J. Amer. Chem. Soc., 82, 1235 (1960).
7. The Infra-red Spectra of Complex Molecules, L. J. Bellamy, Methuen and Co., London, 2nd edition B, 1958, p. 132.