¹H AND ¹H-{²⁹Si} NMR SPECTRA OF DIMETHYLAROXYSILANES

UDC 543.422.25:547.1'128

M. F. Larin, É. I. Dubinskaya, M. G. Voronkov, and V. A. Pestunovich

The shielding of the ²⁹Si nuclei in molecules of type $(CH_3)_3SiZC_6H_4X$, where Z = 0(I) [1-3], S (II) [3], or NH [3, 4], is more sensitive to the effect of the X substituents than in the molecules (CH₃)₃SiC₆H₄X (IV) [5]. This increase in the sensitivity of the ²⁹Si NMR can be explained in two ways. On the one hand, it can reflect an actually greater change in the electron density on the Si atom in molecules (I)-(III) when compared with the corresponding trimethylaroxysilanes,[†] and, on the other hand, the discussed phenomenon can be caused by a change in other characteristics of these molecules, which determine the shielding of the ²⁹Si nucleus. It is possible that an increase in the range of change in the electron density on the Si atom and, consequently, the δ Si values of compounds (I)-(III) is determined by involvement of the Z bridge atom in the polar conjugation, which is controlled by the induction effect of the substituent $R = C_6H_4X$, with either the substituent itself, or with the reaction (indicator) center, or simultaneously with both of them. Previously [2] it was shown that the ²⁹Si chemical shifts (CS) of the trimethylaroxy-, trimethylacyloxy- [6], and trimethylalkoxysilanes [7] obey the same dependence on the aliphatic induction constants (σ^*) of the substituents R [R = C₆H₄X, C(0)X, and $(CH_2)_n X].$

$$\delta Si = (15.38 \pm 0.14) + (4.66 \pm 0.07)\sigma_{R}^{*}, S = 0.33, r = 0.998$$

This proves that the electronic interactions of SiOR, which cause an increase in the sensitivity of δ Si, are independent of the nature of the R substituent. Consequently, a high sensitivity of the ²⁹Si resonance to the effect of the R substituent in the SiOR fragment cannot be explained by the effect of the conjugation of the bridge oxygen with the π -electron system of the R substituent [C₆H₄X and C(O)X]. Common for the indicated three types of substituents can be their induction effect. In order to further study the nature of the increase in the sensitivity of the ²⁹Si resonance observed for the aroxysilanes we obtained the ¹H and ¹H-{²⁹Si} NMR spectra of the dimethylaroxysilanes H(CH₃)₂SiOC₆H₄X (V).

The values of the CS of ¹H and ²⁹Si, and of the SSCC (spin-spin coupling constants) J_{Si-H} , of the dimethylaroxysilanes are given in Table 1. The ²⁹Si CS of the dimethyl-aroxysilanes (V), as well as of the trimethylaroxysilanes (I), are highly sensitive to the effect of the X substituents when compared to the trimethylarylsilanes:

in the (V) series $\delta Si = 4.16 + (3.34 \pm 0.64)\sigma$, $S_0 = 0.55$, r = 0.925in the (I) series $\delta Si = 18.30 + (4.94 \pm 0.86)\sigma$, $S_0 = 0.35$, r = 0.978in the (IV) series $\delta Si = -4.30 + (2.72 \pm 0.32)\sigma$, $S_0 = 0.14$, r = 0.991.

The ${}^{1}J_{Si-H}$ SSCC are linearly dependent on the σ_{p} constants of the X substituents:

$$J_{\text{Si-H}} = (207.49 \pm 0.18) \pm (3.47 \pm 0.45)\sigma_{p}, S_{0} = 0.38, r = 0.954$$

For the dimethylarylsilanes $H(CH_3)_2SiC_6H_4X$ (VI) the analogous function is characterized by a higher value of ρ [9].

$${}^{1}J_{\text{Si-H}} = 188.5 + 6.72\sigma_{p}, r = 0.99$$

It is known that if the Si atom in molecules of type RR'R"SiH is linked to only one electronegative substituent, then the ${}^{1}J_{Si-H}$ values are linearly dependent on the sum of the induction effects of the substituents [10]. Consequently, a comparison of the slopes

[†]Here and subsequently the expression "change in the electron density" must be understood to mean the change in both the magnitude and the spatial distribution of the electron density.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1885-1887, August, 1981. Original article submitted November 8, 1980.

X	vH(SiH), Hz	vH(SiCH₃), Hz	ðsi, ppm	^{1J} Si–H, Hz
H	281,6	$26,3 \\ 24,4 \\ 25,6 \\ 27,4 \\ 26,9 \\ 26,5 \\ 33,5 \\ $	3,47	207,4
4-CH ₂	278,5		3,70	207,0
4-F	277,9		4,76	207,4
4-Cl	279,0		5,75	208,0
4-Bn	279,9		4,92	209,2
4-I	279,6		4,86	208,7
3-NO ₂	285,8		6,94	209,8

TABLE 1. Parameters of NMR Spectra of Dimethylaroxysilanes H(CH₃)₂SiOC₆H₄X

of the functions ${}^{i}J_{Si-H} = f(\sigma_p)$ for (V) and (VI) indicates that the effect of the substituent R = C_6H_4X is weakened by the oxygen atom. Consequently, the possible p,m or σ ,m conjugations between the bridge oxygen and the aromatic substituent R = C_6H_4X do not increase the -I induction effect of the latter. This conclusion probably can also be extended to the other bridge atoms (Z = S, NH) in the (CH_3)_3SiZC_6H_4X molecules.

We will now analyze the possibility of increasing the sensitivity of the ²⁹Si resonance in molecule of type $Y(CH_3)_2SiZC_6H_4X$ (Y = H, CH₃, Z = O, NH, S) due to the conjugation interaction of the Z atom with the Si atom. The important role of conjugation effects of this type in the studied series of compounds is indicated by the increase in the range of change in the CS of the H-Si protons of dimethylaroxysilanes (V) when compared with those known for the dimethylarylsilanes (VI) [9].

> for (V) vH (Hz) = $396.21 + (4.4 \pm 0.94)\sigma_I + (17.58 + 1.53)\sigma_R$, $S_0 = 0.6$, r = 0.987, for (VI) vH (Hz) = $353.05 + (2.72 \pm 1.72)\sigma_I + (6.09 \pm 1.64)\sigma_R$, $S_0 = 0.69$, r = 0.935

In these compounds the contributions of the anisotropy of the benzene ring to the shielding of the H-Si protons are small and not in a condition to noticeably change the range of change in their CS. This means that in the $H(CH_3)_2SiOC_6H_4X$ molecules the effect of the X substituents on the electron density of the H atom adjacent to the Si is greater than in the dimethylarylsilanes. The CS of the protons of the Si-methyl groups are also somewhat more sensitive to the effect of the substituents $R = C_6 H_4 X$ in the dimethylaroxysilanes than in the dimethylarylsilanes [9]. Consequently, it may be assumed that also on the Si atoms in the dimethylaroxysilane molecules the electron density changes as a function of the nature of the X substituent in a broader range than in the dimethylarylsilanes. Since the presence of an oxygen bridge between the Si atom and the substituent $R = C_{s}H_{4}X$ weakens the induction effect of the latter, a greater change in the electron density on the Si atom in aroxysilanes can be due to a more marked change in the π components* (due to the conjugation effects in the Si-O fragment). This can probably also explain the greater sensitivity of the ²⁹Si CS to the effect of the substituent $R = C_6H_4X$ in aroxylsilanes when compared with arylsilanes. However, it is possible that the conjugation of the Z bridge atom with the Si atom is not the sole reason for the observed expansion in the range of the ²⁹Si CS of compounds of type Y(CH₃)₂SiZC₆H₄X. It is not excluded that the observed phenomenon is caused, for example, also by the local change in the average excitation energy of the molecule when the Z heteroatom is varied [11]. This can lead to a substantial increase in the sensitivity of the 29Si shielding constant to a change in the electron density on the Si atom.

EXPERIMENTAL

The PMR and ${}^{1}H{-}{{}^{29}Si}$ spectra were obtained on a BS-487C NMR spectrometer, which was equipped with a universal attachment for heteronuclear double resonance [8]. The compounds were studied as 15-20% CCl₄ solutions. The accuracy of determining the chemical shifts was: ${}^{1}H \pm 0.01$ ppm, ${}^{29}Si \pm 0.1$ ppm, and ${}^{1}J_{Si-H} \pm 0.1$ Hz.

The dimethylaroxysilanes $H(CH_3)_2SiOC_6H_4X$ were obtained in $\sim 100\%$ yields by reacting the appropriate phenols with tetramethyldisilazane by the following scheme:

 $2XC_6H_4OH+[H(CH_3)_2Si]_2NH\rightarrow 2H(CH_3)_2SiOC_6H_4X+NH_3, X=H, CH_3, F, Cl, Br, I, NO_2.$

*The quantity ${}^1J_{\text{Si-H}}$ in these compounds is insensitive to the π effects.

The structure of the synthesized compounds was confirmed by the NMR and IR spectral data, and also by the elemental analysis.

CONCLUSIONS

1. The ²⁹Si chemical shifts of substituted dimethylaroxysilanes are more sensitive to the effect of the X substituent than are the substituted dimethylarylsilanes.

2. The insertion of an oxygen bridge atom leads to a weakening of the induction effect of the C_6H_4X substituent.

3. An increase in the sensitivity of shielding the ²⁹Si nuclei is probably caused either by the conjugation interactions of the O bridge atom with the Si atom or by the local change in the average excitation energy of the molecule when going from $H(CH_3)_2SiC_6H_4X$ to $H(CH_3)_2SiOC_6H_4X$.

LITERATURE CITED

- 1. R. L. School, G. E. Maciel, and W. K. Musker, J. Am. Chem. Soc., <u>94</u>, 6376 (1972).
- J. Schraml, R. Ponec, V. Chvalovsky, H. Jancke, G. Engelhardt, H. Kriegsmann, M. F. Larin, V. A. Pestunovich, and M. G. Voronkov, J. Organomet. Chem., <u>178</u>, 55 (1979).
- 3. M. F. Larin, Dissertation, Irkutsk (1977).
- V. A. Pestunovich, N. F. Larin, A. E. Pestunovich, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1977</u>, 1445.
- 5. C. R. Ernst, L. Spialter, G. R. Buell, and D. L. Wilhite, J. Am. Chem. Soc., <u>96</u>, 5375 (1974).
- 6. W. McFarlane and J. M. Seaby, J. Chem. Soc. Perkin Trans. 2, 1972, 1561.
- 7. J. Schraml, J. Pola, H. Jancke, G. Engelhardt, M. Cerny, and V. Chvalovsky, Coll. Czech. Chem. Commun., 41, 360 (1976).
- 8. M. F. Larin and B. Z. Shterenberg, Zavod. Lab., <u>45</u>, 721 (1979).
- 9. Y. Nagou, M. A. Ohtsuki, T. Nakano, and H. Watanabe, J. Organomet. Chem., <u>35</u>, 81 (1972).
- 10. V. P. Mileshkevich and N. F. Novikova, Dokl. Akad. Nauk SSSR, 223, 916 (1975).
- 11. B. M. Lynch, Can. J. Chem., 55, 541 (1977).

HYDROXYMERCURATION-DEMERCURATION OF (±)-PINOL

UDC 542.91:547.598.5:546.49

B. A. Arbuzov, Z. G. Isaeva, and V. V. Ratner

It is known that pinol (I) in electrophilic substitution reactions reacts both with a retention of the carbon structure (KMnO₄ [1,2], OsO₄ [2], peracids [3], nitrosyl chloride [2, 4]), and with rearrangement (HOC1 [2], Br₂ [2], NBS [5]). We studied the hydroxymercuration-demercuration of (\pm)-pinol (I) in orger to ascertain if this reaction, proceeding without rearrangement, can be used to synthesize the difficultly available stereoisomeric 2 α , 3 β - and 2 β , 3 β -caranediols [6].

On the basis of the data on the regio- and stereoselectivity of hydroxymercurationdemercuration reactions [7-11] the formation of $(\pm)-4\beta$ -hydroxypinol, with a syn orientation of the hydroxyl group relative to the pinol bridge, could be expected.

As it was found, in the case of (\pm) -pinol (I) this reaction is very slow: Even after keeping the reaction mixture at $\sim 20^{\circ}$ C for 14 days the reaction products contain 20% of unchanged (I). The reaction of (I) with a stronger electrophilic reagent like Hg(OCOCF₃)₂ is somewhat faster, but the amount of unreacted (I) in the reaction mixture remains the same after 24 h.

According to the PMR spectrum, the main reaction product has a pinol structure. The PMR spectrum (δ , ppm) has the signals of a gem-dimethyl group at the C atom attached to O

A. M. Butlerov Scientific-Research Chemical Institute of the V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1888-1890, August, 1981. Original article submitted November 10, 1980.