

100 Megacycle nuclear magnetic resonance spectra of tetra-*trans*-propenyltin, *trans*-propenyltrimethylgermane and *trans*- β -stryryltrimethyltin*

In recent studies on the preparation of propenyl and β -stryryl organometallic compounds¹⁻⁴ we were faced with the problem of structure assignment for several sets of geometrical isomers. Infrared spectroscopy was used to make initial assignments, with a band near 980 cm⁻¹ being taken as characteristic of the *trans* isomer⁵. These assignments were confirmed in some cases by NMR spectra, since it has been well established that *trans* coupling between olefinic protons is inevitably greater than *cis* coupling^{6,7}. Ultraviolet spectroscopy also was used to confirm isomer assignments in the case of two β -stryryl derivatives¹.

For several of our compounds the NMR spectra were exceedingly complex due to the small chemical shifts between the olefinic protons. As a result, coupling constants could not be obtained accurately, and isomer assignments rested mainly on infrared spectral evidence¹. We have now obtained 100 Mc NMR spectra of three of these compounds and have been able to determine coupling constants in two cases. Our interest in this problem was revived by a recent Russian report⁸ on tetra-*cis* and tetra-*trans*-propenyltin. The physical constants reported by these authors were in good agreement with those reported by us previously¹, but there were significant differences in the infrared C=C stretching frequencies.

Tetra-trans-propenyltin

In the 60 Mc. spectrum of this compound the complexity of the olefinic signals prevented a first order analysis, although the *trans* coupling constant was estimated as 19.2 cps¹. In the 100 Mc. spectrum, the α proton appeared as a distinct doublet ($J = 18.0$ cps) with peaks at 5.97 and 5.79 ppm. The β proton appeared as two sets of three peaks, with $J(\text{CH}_3\text{-H}_\beta) = 5.0$ cps. The low-field set of signals occurred at 6.30, 6.25 and 6.20 ppm, while the high-field set occurred at 6.12, 6.07 and 6.02 ppm. Since first order splitting rules predict that the signal of the β proton should appear as two quartets, it is obvious that one peak is missing in each set of signals. In this case, the relative intensities of the three observed peaks indicated that the fourth peak was on the high field side. The expected peak at 6.15 ppm was obscured by the background noise, and that expected at 5.97 ppm was dominated by the strong α proton signal at that position.

This spectrum was analyzed in detail by the method outlined by Jackman⁹ for an AB system. First, the ABX₃ system was simplified to an AB system by taking the centers of the β proton quartets as the position of a hypothetical doublet. Such an operation is reasonable in view of the large chemical shift between the β proton signals and the coupled methyl group. The calculations revealed that the α proton occurs at 5.92 ppm and the β proton at 6.10 ppm. Since $J(\text{H}_\alpha\text{-H}_\beta) = 18.0$ cps, and $\delta_B - \delta_A = 18.0$ cps, the ratio $J_{AB}/(\delta_B - \delta_A) = 1.0$, a pronounced AB situation. The calculated ratio of the intensity of the inner doublet signal to that of the outer signal was 5.9:1. This ratio is slightly less than that found experimentally (6.1:1), but the agreement seems reasonable when it is recalled that the intensity of the inner signal is increased slightly by the highest field quartet peak of the β proton.

* Part XXI of the series "Vinyl Derivatives of Metals"; for Part XX see ref. 4.

Since the magnitude of the olefinic coupling constant ($J(H_\alpha - H_\beta) = 18.0$ cps) in this isomer is appreciably larger than that previously observed in tetra-*cis*-propenyltin (13.2 cps)¹, the spectrum provides strong supplementary evidence supporting the previous structural assignments. It may be noted that the 100 Mc. spectrum (*trans* isomer) was run in $CDCl_3$, while the 60 Mc. spectrum of the *cis* isomer was obtained in carbon tetrachloride solution. We are, however, unaware of solvent changes producing significant changes in the coupling constant of simple olefinic compounds, and we feel that a direct comparison of these coupling constants is valid.

The methyl group appeared in the 100 Mc. spectrum as a doublet ($J = 5.0$ cps) at 1.85 ppm. Also of interest were two small peaks at 6.41 and 5.53 ppm, symmetrical about the main α proton peak at 5.97 ppm. These signals undoubtedly arise from coupling of the ¹¹⁷Sn and ¹¹⁹Sn isotopes with the α proton, and a coupling constant of 88 cps is indicated. In our previous work¹ the magnitude of this coupling was estimated as 90 cps.

trans-Propenyltrimethylgermane

Here a situation very similar to that of tetra-*trans*-propenyltin was encountered. The α proton appeared as a distinct AB doublet ($J = 18.0$ cps) with peaks at 5.48 and 5.66 ppm. Only three peaks in each of the expected β proton "quartets" were visible, the low field signals occurring at 5.97, 5.92 and 5.87 ppm, the high field signals at 5.79, 5.74 and 5.69 ppm. The shape of these signals indicated that the fourth peak again was on the high field side, and a shoulder was observed on the α proton signal at 5.64 ppm. An AB analysis of the system, identical to that performed for tetra-*trans*-propenyltin, gave the following results: H_α at 5.61 ppm, H_β at 5.76 ppm and the ratio $J_{AB}/(\delta_B - \delta_A) = 1.19$; calculated intensity ratio of doublet peaks: 7.7:1; observed: 8.0:1. The higher observed doublet ratio is in accordance with expectations, since the "inner" doublet peak of the α proton also includes the highest field peak of the β proton quartets. The relative magnitudes of the *trans* and *cis* coupling constants (18.0 and 13.2 cps, respectively) confirm the previous¹ structural assignments.

The methyl group appeared as a doublet ($J = 5.0$ cps) at 1.63 ppm. This position represents a significant shift to higher field relative to the position of the methyl group in the 60 Mc. spectrum, which was taken in CCl_4 solution (1.80 ppm)¹. No explanation of this large shift can be given, and only a very small shift to higher field (0.03 ppm) was observed in the case of tetra-*trans*-propenyltin.

trans- β -Styryltrimethyltin

Although the structure of this isomer was firmly established by both infrared and ultraviolet spectroscopy⁴, the 60 Mc. NMR spectrum did not furnish a coupling constant. In the olefinic region only a single, unsplit peak (with intensity equivalent to two protons) was observed. It was hoped that distinct doublets could be observed at 100 Mc., but again, only a single, unsplit peak, with intensity equivalent to two protons was observed at 6.66 ppm. There was no evidence of the outer peaks of the expected doublets. Thus, *trans*- β -styryltrimethyltin provides an example of the ultimate AB spectrum - two nonequivalent (and undoubtedly strongly coupled) olefinic protons with *identical* chemical shifts. The aromatic protons appeared as complex multiplets between 6.9 and 7.3 ppm.

The NMR spectrum of *trans*- β -styryltrimethyltin also was run at 60 Mc. in

dimethyl sulfoxide, in the hope that a solvent of high polarity might affect the chemical shift of the two olefinic protons to different extents. However, only a single olefinic peak was obtained in this solvent.

Experimental

The preparation of these compounds has been described previously^{1,4}. We are grateful to Dr. REIICHI SUZUKI for samples of all three. The 100 Mc. NMR spectra were recorded on a Varian HA-100 spectrometer. Deuteriochloroform was used as solvent, and all chemical shifts are reported relative to tetramethylsilane. We are indebted to Mr. JERRY HOLCOMB of Varian Associates for obtaining these spectra.

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PRELIMINARY NOTES

Reactions of bis(trimethylsilyl)mercury with organic compounds containing oxygen, nitrogen, or halogen

In extension of our work on reactions of trimethylsilyl radicals¹, we have analysed the products of the thermal decomposition of bis(trimethylsilyl)mercury² in various oxygen-, nitrogen-, or halogen-containing organic solvents. We find that the dominant feature of the behaviour of trimethylsilyl radicals towards such compounds is the ease with which they abstract oxygen or halogen atoms.

When anisole is heated with bis(trimethylsilyl)mercury, the products (identified by gas chromatography) are trimethylsilane, tetramethylsilane, hexamethyldisilane, hexamethyldisiloxane, and phenoxytrimethylsilane, and it seems that silyl radicals can displace methyl or phenyl radicals from oxygen:

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