Proton Magnetic Resonance of Thiophenes

XII. Chemical Shifts and Coupling Constants of Thienyllithium Derivatives

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The NMR-spectra of thienyllithium derivatives in ethyl ether have been studied. Somewhat unexpectedly, the lithium atom causes a downfield substituent shift, especially of the *ortho*-hydrogens. Also, the well established intervals of the thiophenic coupling constants become invalid. The lithium derivatives show smaller coupling constants than "normal" thiophenes.

During recent years the proton resonance spectra of organolithium compounds and other organometallic compounds have been studied with the hope of obtaining a better understanding of the nature of the carbon-metal bond and the molecular structure of these compounds. (For a short review *cf.* Ref. 1). Mass spectral studies of ethyllithium indicate that it exists as a hexamer and tetramer in the vapour phase at about 90°C,[2] while IR-spectra and proton and lithium NMR-spectra indicate that ethyllithium exists as a single species in hydrocarbon solvents, probably as a hexamer.[3]

Dailey and Shoolery [4] have clearly demonstrated the existence of a linear correlation between the internal shifts in ethyl derivatives and the electronegativity of the substituent atom. For organometallic compounds Narasimhan and Rogers [5] found the relation electronegativity $= 0.62$ (δ CH$_3$—δ CH$_2$) $+$ 2.07.

This linear relationship, and a similar one for methyl derivatives, have also been used to determine the previously controversial electronegativities of the group IV-B elements.[5,6] In the NMR-spectrum of ethyllithium [3] the strongly electron-donating effect ($+I$-effect) of the lithium is strongly noticeable, the CH$_2$ resonance occurring 2.19 ppm towards higher field than the CH$_3$ resonance. Application of the above relation would lead to an electronegativity of 0.7 for lithium, which is even smaller than that usually assumed (0.9—1.0). Some of the variance has been ascribed to the possibility that the

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methylene carbon is involved in electron deficient bridge bonding, which should cause increased shielding of the methylene group.[3]

The PMR-spectrum of vinyllithium in ether solution gives rise to a complex ABC-spectrum, which has been analysed.[7] The assignments of the three resonances were based on the observation by Banwell et al.[8] that gem, cis, and trans coupling constants in the vinyl group show a clear linear decrease with increasing electronegativity of the substituent. In accordance with this the analysis of the vinyllithium spectrum led to $J_{trans} = 23.9$ c/s, $J_{cis} = 19.3$ c/s, and $J_{gem} = 7.1$ c/s. In common organic compounds these coupling constants are of the order of 17 c/s, 10 c/s, and 1 c/s, respectively. Although Johnson et al.[7] did not measure the chemical shifts of vinyllithium relative to ethylene or propylene, they noticed that the resonance of the proton at the same carbon as the lithium occurred at the lowest field. Considering the strongly electron-donating properties of the lithium atom and the results obtained with ethyllithium, this is rather unexpected and surprising, indicating that other factors than local charge densities strongly contribute to the chemical shifts of vinyllithium.

In connection with a study on the kinetics of the metalation of thiophene with butyllithium, which we intended to follow by NMR, we studied the PMR-spectra of 2-thienyllithium, 3-thienyllithium, 5-bromo-2-thienyllithium, 3-bromo-2-thienyllithium, 4-bromo-2-thienyllithium, and 4-bromo-3-thienyl-lithium in ether solution. The spectrum of 2-thienyllithium was obtained at room temperature, while all the other were recorded at −60°C immediately after their preparation in order to avoid rearrangement to the thermo-dynamically more stable lithium derivatives.[9]

All of the bromothienyllithium derivatives gave simple AB- or AX-spectra, while 2-thienyllithium gave an ABX-spectrum from which shifts and coupling constants easily could be obtained. Only 3-thienyllithium gave a strongly coupled spectrum, which has not been analysed. The chemical shifts and

Table 1. Chemical shifts (τ-values) and coupling constants of thienyllithium derivatives and some other thiophenes in ether solution.

Substituent	Chemical shifts				J_{23}	J_{24}	J_{25}	J_{34}
	H-2	H-3	H-4	H-5				
None	2.67	2.92	2.92	2.67	—	—	—	—
2-Li	—	2.48	2.82	2.34	4.3	0.5	—	2.8
3-Li	Strongly coupled. Largest peaks at 2.31 and 2.94							
2-Br	—	2.96	3.17	2.74	5.5	1.7	—	3.7
3-Br	2.68	—	2.99	2.68	—	—	—	—
5-Br, 2-Li	—	2.71	2.94	—	—	—	—	2.6
4-Br, 2-Li	—	2.73	—	2.44	—	0	—	—
3-Br, 2-Li	—	—	2.96	2.41	4.4	—	—	—
4-Br, 3-Li	2.68	—	—	2.73	—	—	2.7	—
2-Br, 5-Br	—	3.12	3.12	—	—	—	—	—
2-Br, 4-Br	—	2.98	—	2.66	—	1.7	—	—
2-Br, 3-Br	—	—	3.08	2.62	5.8	—	—	—
3-Br, 4-Br	2.51	—	—	2.51	—	—	—	—

coupling constants are collected in Table 1 and for comparison the parameters for thiophene and the mono- and dibromothiophenes in ether solution are also given.

The first striking observation is that the well-established intervals for the four coupling constants in thiophenes,[10] which have been so useful for structure determination of mono- and disubstituted thiophenes, become invalid. In thiophenes with "common" organic substituents, $J_{34} = 3.45-4.35$ c/s, $J_{45} = J_{23} = 4.90-5.80$ c/s, $J_{35} = J_{24} = 1.25-1.70$ c/s, and $J_{25} = 3.20-3.65$ c/s. In the lithium derivatives, we observe $J_{34} = 2.6-2.8$ c/s, $J_{45} = J_{23} = 4.3-4.4$ c/s, $J_{35} = J_{24} = 0-0.5$ c/s, and $J_{25} = 2.7$ c/s. It is interesting to note that in thiophenes lithium has an effect on the magnitude of the coupling constants opposite to its effect in vinyl compounds. There is, however, a connection between the magnitude of thiophenic coupling constants and the electronegativity of the substituents. It has for instance been observed that J_{34} is largest in 2,5-disubstituted thiophenes having two electron-attracting substituents. It has also recently been found that in 2,3-difluorothiophene, J_{45} is as large as 6.6 c/s.[11]

The effect of the lithium on the chemical shifts of the proton are very surprising. Comparing the shifts of 2-thienyllithium with those of thiophene it is evident that the lithium shifts the 3-hydrogen resonance 0.44 ppm, the 4-hydrogen resonance 0.10 ppm and the 5-hydrogen resonance 0.33 ppm towards *lower* field. Similar comparison of the chemical shifts of 4-bromo-2-thienyllithium and 3-bromo-2-thienyllithium with those of 3-bromothiophene indicate that the resonance of the proton positioned "meta" to the lithium atom is only shifted slightly towards lower field, while those *"ortho"* or *"para"* are shifted about 0.25 ppm towards lower field.

Similar shifts are observed in 5-bromo-2-thienyllithium compared to 2-bromothiophene. An exception is 4-bromo-3-thienyllithium which shows no shifts compared to 3-bromothiophene.

When we completed this work we noticed the recent work of Ladd [12,13] on the NMR-spectrum of phenyllithium in ether. The five protons gave a complex spectrum even at 100 Mc/s. The analysis of this spectrum led, interestingly enough, to normal coupling constants. However, he found that while the *ortho*-hydrogen resonances occurred 0.74 ppm towards lower field from benzene, the *meta* and *para* resonances were shifted 0.23 ppm and 0.3 ppm upfield. In order to explain the unexpected downfield shift of the *ortho* hydrogen resonances, Ladd suggested that the magnetic anisotropy of the carbon-lithium bond causes such a large paramagnetic shift that it outweighs the strong inductive effect of the lithium. At the *meta* and *para* positions, due to the greater distance involved, the contribution from the anisotropy effect is smaller and the inductive electron-donating effect increases the shielding of this proton either directly or through polarization of the π-electrons. However, the somewhat different behaviour of the thienyllithium derivatives makes us believe that the conditions are more complicated and that the chemical shifts of the lithium derivatives cannot be discussed only in terms of these contributions, first introduced by Saika and Slichter.[14] It is also questionable whether the carbon-lithium bond can be so highly anisotropic. The structure of aryllithium compounds in ether solution is not known with certainty. Wittig *et al.*[15]

have suggested that phenyllithium exists in this solvent as a highly solvated dimer. It is therefore possible that this complex has such a geometric arrangement that the ringcurrent in each ring influences the chemical shifts of the protons in the other ring.

We wish to report this rather unexpected and unpredictable behaviour of the chemical shifts and coupling constants of thienyllithium derivatives, which we must admit that we do not completely understand, but we hope that more detailed investigations will solve these interesting problems.

EXPERIMENTAL

Ethereal solutions (8—10 wt. %) of the 3-thienyllithium and the bromo-thienyl-lithium derivatives were prepared at —70°C as described earlier.[9] Samples were quickly drawn up into evacuated NMR-tubes, sealed off and kept at —70°C until the NMR-spectra were measured at —60°C (within 5 min). 2-Thienyllithium[16] was prepared at room temperature and measured at the working temperature (36°C) of the NMR-apparatus. The NMR-spectra were obtained with a Varian A-60 high resolution spectrometer with a V-6057 variable temperature accessory.

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