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Preliminary communication

FACILE CONTROL OF PREFERRED GEOMETRY OF PENTADIENYLPOTASSIUM BY CHANGING THE MEDIUM: "U"-SHAPED IN SOLUTION AND "W"-SHAPED IN THE SOLID STATE

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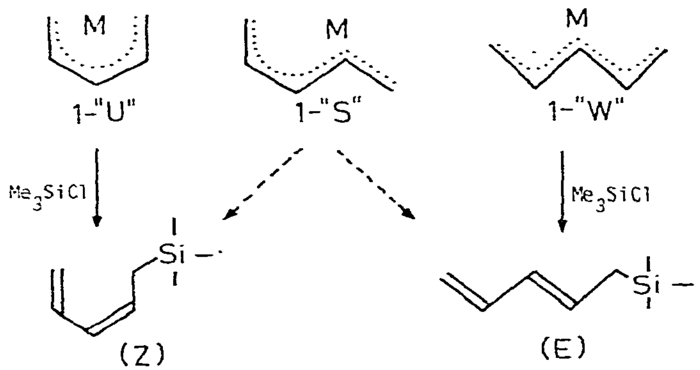
Summary

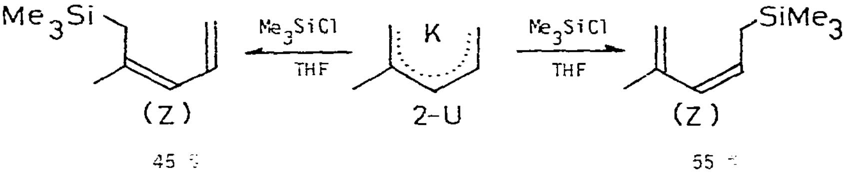
The structure of pentadienylpotassium in THF was determined to be the U-shaped by chemical trapping with chlorotrimethylsilane and from the ^{1}H NMR spectrum. The results of trimethylsilylation of pentadienylpotassium in the solid state indicate that it assumes the W-shaped structure in the crystalline state.

EH- and SCF-MO calculations on the geometry of open chain pentadienyl anions have indicated that the "U"-shaped structure is favored over the "W"- or "S"-shaped [1] and that the highest electron density is on the C(3). However, Dewar et al. recently claimed, based on MNDO calculations, that the "W"-shaped conformation is the most stable [2]. Experimental evidence has been interpreted to indicate that pentadienyl- [3], hexadienyl- [4], and 3-methylpentadienyllithium [4] in THF, and pentadienyl- [5] and hexadienylpotassium [6] in liquid ammonia exist preferentially as the W-shaped anions. Schlosser recently reported evidence for the U-shaped structure for the first time in the cases of 2-methyl- and 2,4-dimethyl-pentadienylpotassium in THF based on the geometry of the pentadien-1-ols derived from the anions [7].

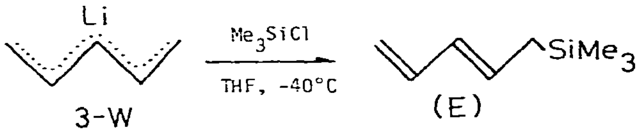
We have investigated the regioselective trimethylsilylation of the parent pentadienylpotassium 1 in ethereal solution and in the solid state in order to evaluate these MO predictions and have found a facile method of control of the preferred geometry of 1 by changing the medium. The pure crystalline pentadienyl anion salts used in this work were prepared as previously described [8]. Trimethylsilylation of 1 with chlorotrimethylsilane in THF solution gave (*Z*)-2,4-pentadienyltrimethylsilane regioselectively (88% yield at 30°C and 98% at −40°C), in line with the protolysis [8] of 1 in THF which



gave 95—97% of (*Z*)-1,3-pentadiene. The exclusive production of the (*Z*)-isomer shows the presence of a single torsional isomer, i.e., the U- or S-shaped anion. If trimethylsilylation occurs equally on both terminals (C(1) and C(5)) of pentadienyl group, the structure of **1** is readily assigned to the U-shape because the S-shaped anion should produce just one pair of (*Z*)- and (*E*)-isomers. To confirm this postulate, trimethylsilylation of 2-methylpentadienylpotassium **2** was examined and nearly equal amounts (11/9) of 4-methyl-(*Z*)-2,4-pentadienyltrimethylsilane and 2-methyl-(*Z*)-2,4-pentadienyltrimethylsilane were obtained as evidenced by gas chromatographic analysis and by decoupled ^1H NMR spectra and/or NOE experiments. Thus, trimethylsilylation occurs at both termini in good accordance with the dimethoxyboration-oxidation of **2** as reported by Schlosser. Hence, the above-mentioned extreme preference for



(*Z*)-2,4-pentadienyltrimethylsilane indicates the U-shaped structure for the parent pentadienylpotassium **1**. Dimethoxyboration-oxidation of **1** in THF has found recently to give (*Z*)-pentadien-1-ol regioselectively [9]. We have examined the trimethylsilylation of pentadienyllithium, **3**, which is known to assume the W-shaped structure [3]. The expected (*E*)-isomer was obtained in 98% yield by reaction in THF at -40°C*. A ratio of (*E*)- to (*Z*)-isomer is 98/2. No isomerization of (*Z*)- to (*E*)-2,4-pentadienyltrimethylsilane or of the (*E*)- to the (*Z*)-isomer occurred during the procedure. The opposite geometry observed between **1** and **3** may be rationalized by regarding **1** as composed of contact ion pairs and **3** of strongly solvated (or solvent-separated) ion pairs



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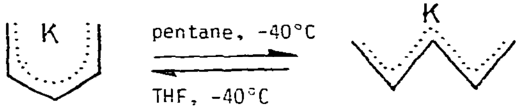
*See also ref. 12 and 14.

since the solvation of 1 by THF is weak while that to 3 is very strong as confirmed previously [8].

Surprising was the finding that 1 in the solid state (quantitative precipitation of 1 occurred by the addition of an excess pentane, 10 mol per mol of THF, to the THF solution at –40°C) produced (*E*)-2,4-pentadienyltrimethylsilane predominantly (75—85%) in sharp contrast to the result obtained in solution. A suspension of THF-free pentadienylpotassium, which was prepared by heating the crystals of 1 in vacuo [8], gave the (*E*)-isomer quantitatively (98%) by trimethylsilylation at –40°C in pentane and (*E*)-1,3-pentadiene (99%) by hydrolysis at 0°C in octane. Yields are 95% in both cases. Thus, the production of (*E*)-isomer with extreme regioselectivity indicates the W-shaped structure for 1 in the crystalline state. The geometry of the pentadienylpotassium in the solid state is probably controlled by the mode of packing in the crystal lattice, although X-ray analysis of 1 with good single crystals gave insufficient data to warrant a definite conclusion on the geometry in the crystalline state.



1-U (in solution) 1-W (in the solid state)

Attempts to analyze the ^{1}H NMR spectrum of 1 have failed because the signals of the protons on C(1), C(3) and C(5) overlapped heavily. Direct evidence for the U-shaped structure of 1 in solution has now been obtained from the NMR spectrum of the 1,1,5,5-tetradeuterated derivative (Fig. 1). The proton—proton coupling constant, J_{23}, which is required for the assignment of the geometry is determined to be 8.7 Hz below –30°C (9.1 Hz at 60°C and constant below –30°C, showing the rotation around the C(2)—C(3) is almost frozen). This value corresponds well to the *cis*-coupling constant (8.3—9.1 Hz) [6,10] observed for alkyl-substituted allylic potassium compounds. Hence the spectrum is reasonably explained as the "U"-shaped structure. The *trans*-coupling constant is known to be ca. 13 Hz [10]. The ^{13}C NMR spectrum of 1 in THF below –30°C, which shows three signals at 79.2, 137.8 and 79.6 ppm downfield from external TMS assignable to C(1)(C(5)), C(2) and C(3) respectively, also supports the U-shaped structure. The magnitude of the J_{23} values for the corresponding rubidium and cesium derivatives (8.9 and 8.7 Hz at 38°C in THF, respectively) and the geometry of the products obtained by trimethylsilylation in THF or pentane are essentially the same as those for 1. It should be noted that the geometry of 1-methylallyl-sodium, -potassium and -cesium was reported recently by Bartmess to be >90% *cis* in solution and predominantly *trans* in the gas phase [11].

The control of preferred geometry of a series of pentadienyl anions thus has been realized by changing the counter cation and the medium rather than the substituent on the pentadienyl group. Such ready control is valuable for organic syntheses utilizing this unique reagent. Lewis acid-catalyzed regioselective addition of 2,4-pentadienyltrimethylsilane to carbonyl compounds [12,13]

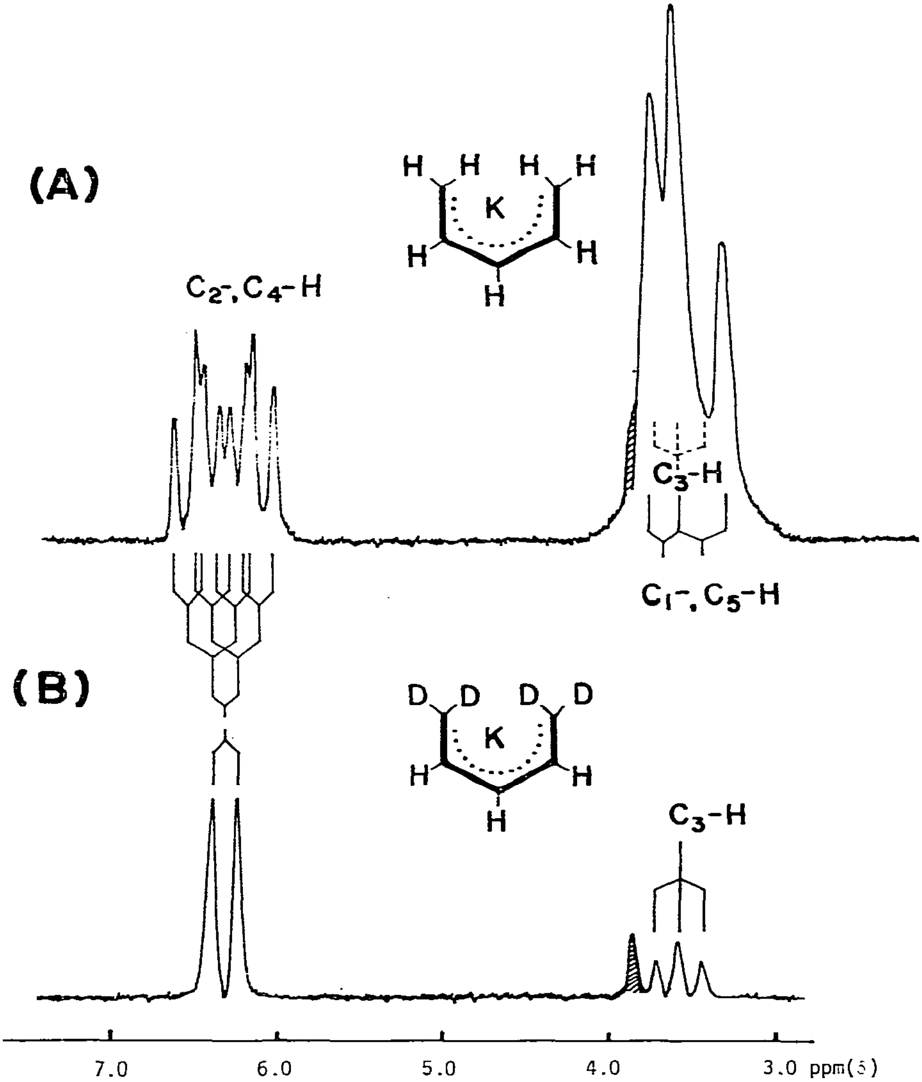


Fig. 1. ^{1}H NMR (100 MHz) spectra of C_5H_7K (A) and $C_5H_3D_4K$ (B) in perdeuterotetrahydrofuran at −30°C. *Shaded peak indicates THF signals contained in solvent.*

leading to dienyl alcohols, reaction of pentadienyltrimethylsilane with nucleophiles [14] and the reaction of a series of pentadienyl anions with metal halides [15,16] should be noted.

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