An Improved Synthesis of Sodium and Potassium Cyclopentadienide

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Summary: Sodium and potassium cyclopentadienide were obtained in an improved synthetic procedure. They were prepared in a one-pot synthesis directly by reaction of alkali metals with neat dicyclopentadiene at elevated temperature. The products precipitated as white powders and were isolated by filtration. The excess of dicyclopentadiene can be recycled. The new reaction procedure provides a much more convenient access to the products, no dry solvents such as THF or decahydronaphthalene are needed, and no colored impurities are observed.

Introduction

Sodium and potassium cyclopentadienide are important reagents in organometallic chemistry, having been used to prepare innumerable cyclopentadienyl complexes.[1] Potassium cyclopentadienide, KCp, was first reported about 100 years ago by J. Thiele, who reacted potassium metal with cyclopentadiene in benzene.[2] Today KCp is generally made by deprotonation of cyclopentadiene either with potassium metal in organic solvents such as THF and benzene or in liquid ammonia (eq 1).[3,4] Also, the deprotonation may be effected with KH[5] or KOH.[6] Fifty years after the first synthesis of KCp the analogous sodium compound, NaCp, was reported by the groups of E. O. Fischer[3] and K. Ziegler.[7] Today NaCp is generally obtained, like KCp, by deprotonation of cyclopentadiene with sodium metal, NaH, NaO*t*Bu, or NaOH (eq 1).[4,6,7] All the reactions described above have in common that *monomeric* cyclopentadiene is used as starting material. Since monomeric cyclopentadiene is not stable at room temperature, it usually is freshly prepared by a thermal retro-Diels−Alder reaction from the commercially available dicyclopentadiene (eq 2). Little effort has been expended to avoid the lengthy thermal retro-Diels−Alder reaction. To the best of our knowledge,[8] there is only one report in the literature in which NaCp was prepared directly from dicyclopentadiene, by a reaction in an autoclave at elevated pressure or in an iron can at normal pressure from dicyclopentadiene and sodium metal in decahydronaphthalene at 170 °C.[7] An analogous procedure for KCp has, to the best of our knowledge, not been reported.[8] Surprisingly, the convenient preparation of NaCp from dicyclopentadiene was not been developed further. Standard textbooks on synthetic procedures[4] and organometallic chemistry[9] do not report this procedure.

$$\text{eq (1)}$$

$$\text{eq (2)}$$
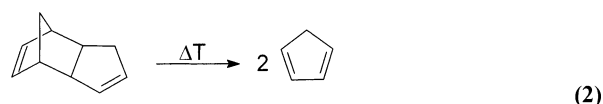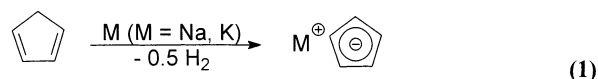
We report here an improved synthesis of NaCp and KCp. Both compounds were obtained directly by the reaction of dicyclopentadiene with the respective alkali metal without solvent.

Results and Discussion

Freshly cut alkali metals were heated in neat dicyclopentadiene at 160 °C. At this temperature the retro-Diels−Alder reaction of dicyclopentadiene to cyclopentadiene takes place. The thus generated cyclopentadiene reacted immediately with the molten alkali metals to give MCp (M = Na, K) and dihydrogen (eq 3).

$$\text{eq (3)}$$
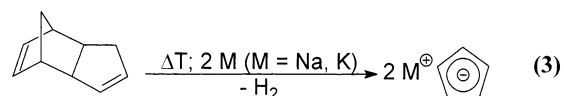
Under these conditions the alkali metals react quantitatively to give MCp. When the akali metal was quantitatively consumed, the dihydrogen evolution stopped. Thus, the endpoint of the reaction can be easily determined by monitoring the dihydrogen evolution. During the reaction, the MCp precipitates as a white solid. The product is isolated as a white powder by filtering the precipitate followed by a subsequent washing with *n*-pentane. The remaining dicyclopentadiene, which decomposed slightly during the reaction, can be

(1) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. *Comprehensive Organometallic Chemisty II*; Pergamon Press: Oxford, 1995; Vol. 1, pp 18, 44; Vol. 4, pp 32, 137, 439, 483, 501, 589; Vol. 6, pp 109, 159, 210, 245; Vol. 7, pp 161, 185, 603; Vol. 8, pp 8, 167, 377; Vol. 9, pp 249, 375, 579.

(2) Thiele, J. *Chem. Ber.* **1901**, *34*, 68.

(3) (a) Fischer, E. O.; Jira, R.; Hafner, K. *Z. Naturforsch.* **1953**, *8b*, 327. (b) Fischer, E. O.; Hafner, W.; Stahl, H. O. *Z. Anorg. Allg. Chem.* **1955**, *282*, 47.

(4) Fehlhammer, W. P.; Herrmann, W. A.; Öfele, K. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Brauer, G., Eds.; Thieme: Stuttgart, 1997; Vol. 3, p 50.

(5) Köhler, F. H.; Geike, W. A.; Hertkorn, N. *J. Organomet. Chem.* **1987**, *334*, 359.

(6) Borisov, A. P.; Makhaev, V. D. *Metalloorg. Khim.* **1989**, *2*, 680.

(7) Ziegler, K.; Froitzheim-Kühlborn, H.; Hafner, K. *Chem. Ber.* **1956**, *80*, 434.

(8) There are many synthetic procedures for MCp in the literature. Even though the literature was checked carefully, we cannot absolutely exclude that we missed a reference.

(9) Elschenbroich, C.; Salzer, A. *Organometallchemie*, 2nd ed.; Teubner: Stuttgart, Germany, 1992; p 373.

recycled without further purification. Alternatively, since dicyclopentadiene is a cheap starting material, it can be discarded at the end of the reaction. Using our improved procedure, the title compounds are obtained much easier and much faster than by the established methods.[4] In the established reaction, when THF is used as solvent, frequently colored products (slight pink to brown) are obtained. In contrast, the MCp always was isolated as a white powder in our new procedure. On dissolving NaCp, which was obtained by our procedure, in THF, sometimes a darkened solution was obtained. However, no impurities were observed in the NMR spectrum. As starting material commercial grade dicyclopentadiene was used without further purification and the MCp products, which were characterized by NMR and elemental analysis, were analytically pure. However, to obtain MCp without any traces of MOH, a predrying of the dicyclopentadiene is suggested.

As expected, the reaction rate depends on the alkali metal. Thus, potassium reacts significantly faster than sodium. Furthermore, the rate depends on the dispersion grade of the liquid alkali metal. Therefore, the reactions always were stirred rapidly. Since lithium metal does not melt under the reaction condition described above, the rate of the reaction is extremely slow. Quantitative conversion was not observed after several days of heating at 160 °C. The reactions were carried out using up to 10 g of the alkali metal (0.43 mol of Na), which usually was sufficient for our purposes.

Experimental Section.

General Considerations. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glovebox. *n*-Pentane was distilled under nitrogen from LiAlH$_4$. Deuterated solvents were obtained from Aldrich Inc. (all 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. All other chemicals used as starting materials were obtained commercially and used without further purification. NMR spectra were recorded on a JEOL JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Elemental analyses were carried out with an Elementar vario EL.

NaCp. Sodium, 10.00 g (0.43 mol), freshly cut, was added to 400 mL of dicyclopentadiene at room temperature. On heating, the solution turned blue (around 35 °C). Before the sodium was completely molten the solution slowly discolored. The mixture was heated for 6 h to 160 °C. On heating, a white solid precipitated. When the akali metal is quantitatively consumed, the dihydrogen evolution stopped. To ensure a quantitative conversation, the heating was continued for another 30 min after the dihydrogen evolution ended. The reaction mixture was filtered, and the white residue washed with three 50 mL portions of *n*-pentane and dried in vacuo. The unreacted dicyclopentadiene (260 mL) was used again for the same reaction. Yield: 38 g (99%). ^{1}H NMR (d_8-THF, 400 MHz, 25 °C): δ 5.60 (s, 5H). ^{13}C NMR (d_8-THF, 100.4 MHz, 25 °C): δ 103.3. Anal. Calcd for C$_5$H$_5$Na (88.08): C 68.18; H 5.72. Found: C 67.69; H 5.43.

KCp. was prepared in a manner similar to NaCp in a 1.32 g (33. 8 mmol) scale of K in 50 mL of dicyclopentadiene. The reaction time was 4 h at 160 °C. Yield: 3.34 g (95%). ^{1}H NMR (d_8-THF, 400 MHz, 25 °C): δ 5.60 (s, 5H). Anal. Calcd for C$_5$H$_5$K (104.19): C 57.64; H 4.84. Found: C 57.32; H 4.35.