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The Isolation and X-ray Structures of Lithium Crown Ether Salts of the Free Carbanions [CHPh₂]⁻ and [CPh₃]⁻

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Numerous publications have shown that salts of delocalized carbanions can exist in solution as ion pairs^{1,2} and their structures, either in solution or solid phase, have generated considerable interest.³ In addition, several groups have shown that crown ethers and glymes may react in solution with the carbanion-alkali-metal complex to form an ion pair having the metal ion coordinated with a polydentate ether.^{4,5} In the crystal phase, the pioneering work of Stucky has resulted in the publication of the structures of several ligand-complexed metal salts of delocalized carbanions.⁶ None of these studies, however, have afforded detailed structures of well-separated noninteracting hydrocarbyl carbanions. Work in this laboratory has shown that crown ethers can be used to obtain crystals of separate anions in other groups of the periodic table, for example, the [Li(12-crown-4)]⁺ salts of [PPh₂]⁻⁷ or [CuPh₂]⁻⁸. We now describe the extension of this technique to the more important carbanions⁹ and give details of the X-ray crystal structures¹⁰ of [Li(12-crown-4)₂][CHPh₂]⁻ (**1**) and [Li(12-crown-4)₂][CPh₃]⁻·THF (**2**).

The isolation of **1** and **2** was as follows. Ten millimoles of CH₂Ph₂ or CHPh₃ were dissolved in THF (100 mL). The addition of *n*-BuLi (6.25 mL of a 1.6 M solution in *n*-hexane) gave an orange color for CH₂Ph₂ and red in the case of CHPh₃. Then 12-crown-4 (3.5 g, 20 mmol) in THF (5 mL) was added dropwise, giving a yellow-orange precipitate of **1** and a slightly cloudy red solution for **2**. Warming completely dissolved the solids and slow cooling to -20 °C afforded the crystalline products **1** and **2**. **1** was isolated as orange needles that turn slowly red on heating, soften at 85 °C, and decompose at 160 °C; **2** was isolated as red needles that decompose at 120 °C. Both **1** and **2** are quite stable

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(10) Crystal data at 140 K with Cu Kα (λ = 1.54178 Å) radiation: **1**, orthorhombic *Pbc*, *a* = 22.797 (4) Å, *b* = 18.332 (3) Å, *c* = 13.708 (2) Å, *R* = 0.077, 347 parameters, 2864 unique observed reflections; **2**, triclinic *P1̄*, *a* = 12.568 (4) Å, *b* = 12.765 (3) Å, *c* = 12.772 (2) Å, α = 78.84 (2)°, β = 78.17 (2)°, γ = 64.06 (2)°, *R* = 0.065, 440 parameters, 4748 unique observed reflections.

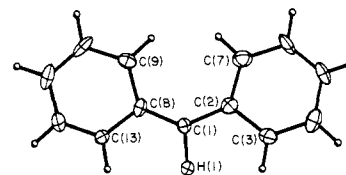


Figure 1. Bond distances (Å) and angles (deg) for **1**: C(1)-C(2) = 1.435 (6); C(1)-C(8) = 1.404 (6); C(2)-C(3) = 1.433 (7); C(3)-C(4) = 1.399 (7); C(4)-C(5) = 1.429 (8); C(5)-C(6) = 1.367 (7); C(6)-C(7) = 1.376 (7); C(7)-C(2) = 1.439 (6); C(2)C(1)C(8) = 132.1 (4); C(1)C(2)C(3) = 117.6 (4); C(1)C(2)C(7) = 119.4 (4); C(2)C(3)C(4) = 123.0 (4); C(3)C(4)C(5) = 120.9 (5); C(4)C(5)C(6) = 116.7 (5); C(5)C(6)C(7) = 123.0 (5); C(2)C(7)C(6) = 123.5 (4). Distances and angles in the C(8) phenyl ring are similar.

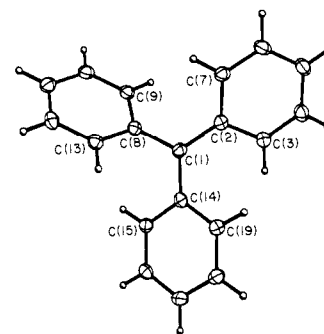


Figure 2. Bond distances (Å) and angles (deg) for **2**: C(1)-C(2) = 1.451 (5); C(1)-C(8) = 1.459 (5); C(1)-C(14) = 1.450 (4); C(2)C(1)C(8) = 119.4 (3); C(8)C(1)C(14) = 118.4 (3); C(2)C(1)C(14) = 122.3 (3). Distances and angles in phenyl rings are similar to those in **3**.

compounds in the absence of air or moisture and THF solutions show little decomposition after several days in the freezer (-20 °C). The solids appear to be indefinitely stable at 0 °C.

The structures of the anions of **1** and **2** are illustrated in Figures 1 and 2.¹¹ The main feature is the planar geometry at each central carbon atom. The coplanarity of the two phenyl rings in **1** and its wide C(2)C(1)C(8) angle of 132.1 (4)° are also noteworthy. The planar cores of **1** and **2** and the total planarity in **1** are manifestations of extensive delocalization. Steric constraints prevent the rings in the anion of **2** from being coplanar and the familiar propeller arrangement is the result. The rings are at angles of 21.3°, 30.3°, and 42.0° (average 31.2°) to the central C(1)C(2)C(8)C(14) plane. There are no really close intramolecular contacts between the central carbon and other atoms in either molecule. For example the closest nonbonded contacts in **2** involve the six ortho hydrogens, which are all approximately 2.7 Å distant.

Structural comparisons are possible between **2** and the previously reported complexes TMEDALi-CPh₃ (**3**)⁶ or its sodium analogue.¹² These complexes are contact ion pairs between [TMEDALi(Na)]⁺ and [Ph₃C]⁻. The main difference is that C(1) in **3** is 0.12 Å out of the plane of C(2), C(8), and C(14), whereas in **2** C(1) has a planar environment. In the more ionic sodium derivative C(1) is also planar. Other bond distances and angles in the molecules are similar.

When **1** and **2** are compared, the C(1)-C(2) and C(1)-C(8) lengths in **1** average slightly shorter than the corresponding C(1)-C(phenyl) distances in **2**. This could be due to better delocalization in coplanar **1** but it also might be a result of greater crowding in **2**. Support for the latter view comes from the C-C distances in the phenyl rings, which average to almost identical lengths in both anions.

An analogous preparation of the unassociated benzyl anion gave a yellow solid, presumably [Li(12-crown-4)]⁺[CH₂Ph]⁻, from ether. Unfortunately, we were unable to isolate crystals due to its rapid decomposition upon addition of THF. Work involving the isolation

(11) The structure of the [Li(12-crown-4)]⁺ cations of **1** and **2** are similar to those in ref. 7.

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of other noninteracting carbanions is in progress.

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Registry No. 1, 95189-24-5; 2, 95189-83-6; CH_2Ph_2 , 101-81-5; CHPh_3 , 519-73-3.

Supplementary Material Available: Tables of data collection and refinement summaries, fractional coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates and stereoviews of the unit cells of 1 and 2 (14 pages). Ordering information is given on any current masthead page.

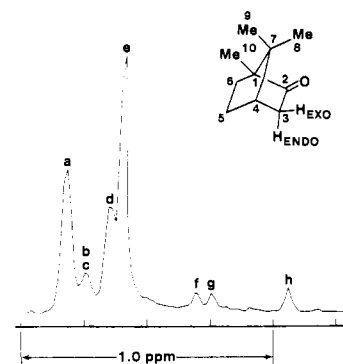


Figure 1. ^2H - and ^1H -decoupled 100.6-MHz ^{13}C NMR of the C-3 and C-4 region of a mixture of 1-4. C-4 peaks: a, 1; b and c, 2 and 3; d, 4. C-3 peaks: e, 1; f, 3; g, 2; h, 4.

NMR Method To Detect Stereospecific Deuterium Labeling at Diastereotopic Methylene Hydrogens: Selective ^1H , ^{13}C Heteronuclear Shift Correlation

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Labeling studies employing NMR detection of hydrogen isotopes are becoming increasingly common because of the insight they offer into biological and chemical mechanisms.¹ The most widely used isotope, deuterium, is routinely observed by changes induced in ^1H NMR spectra,² by direct ^2H NMR,^{2b,3} or by differences in the ^{13}C NMR spectra of carbons that are directly attached to deuterium (e.g., α -isotope shifts)^{3b,4} or two bonds away (β -isotope shifts).⁵ Despite the utility of these methods, determining which of two diastereotopic hydrogens on a methylene group is deuterium labeled is often difficult.⁶ Modern NMR pulse

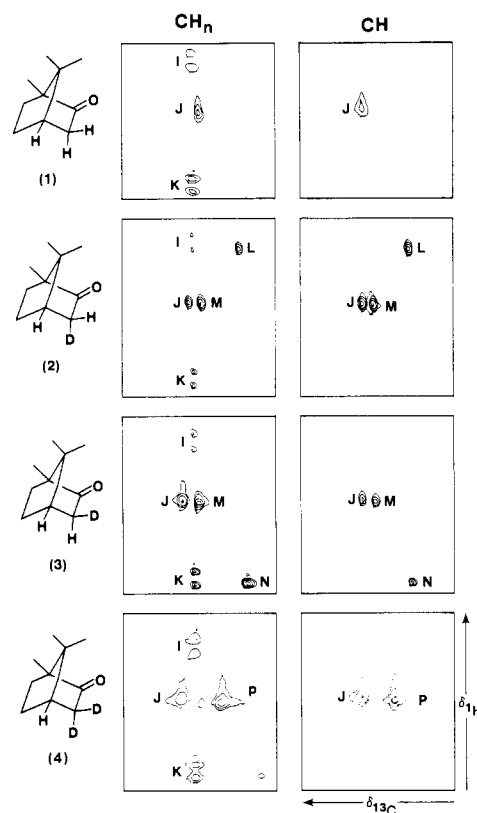


Figure 2. Normal (CH_n) and selective (CH) ^2H -decoupled heteronuclear (^1H , ^{13}C) chemical shift correlation plots of the region containing the C-3 methylene and C-4 methine of camphor. In each plot the chemical shift increases from 1.76 to 2.43 ppm for ^1H on the vertical axis and from 42.76 to 43.93 ppm for ^{13}C (right to left) on the horizontal axis.

methods⁷ have been applied to deuterated systems^{4b,8} but have not yet been tested for such stereochemical analysis. In this paper

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