Organometallic Chemistry

New inter- and intramolecular carbo- and heterocyclizations of 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one and its η^4-rhodiumcyclopentadienyl complex under the action of *n*-buthyllithium: formation of functionally substituted tricyclic spirofuran and bicyclo[2.2.1]heptadiene systems

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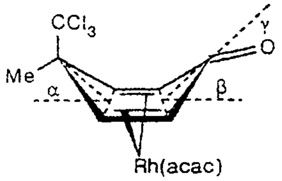
Treatment with Bu^nLi in THF (−60—0 °C) causes 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one and its *exo*-η^4-coordinated (by a RhCp-group) π-diene metal complex to undergo reactions of two new types: intermolecular autocondensation—heterocyclization (affording 3,3-dichloro-3a,4′-dimethyl-4′-trichloromethyl-2,3,3a,6,7,8-hexahydrospiro-[benzofuran-2,1′-cyclohexa-2′,5′-dien]-6-one; 24%) and intramolecular carbocyclization (yielding (η^4-7,7-dichloro-1-hydroxy-4-methylbicyclo[2.2.1]hepta-2,5-diene)(η^5-cyclopentadienyl)rhodium; 77%). Both processes are assumed to involve the formation of an unusual *gem*-CCl_2Li substituted *para*-semiquinoid intermediate, the conformation of the six-membered diene ring of which (planar or a boat-like) governs its subsequent intra- or intermolecular stereospecific carbonyl condensations.

Key words: cyclohexa-2,5-dienones, π-diene complexes of rhodium(I), organolithium compounds, C—halogen bond activation; intra- and intermolecular carbo- and heterocyclizations; use of organometallic derivatives in fine organic synthesis; spirofuranoids; bicyclo[2.2.1]heptadienes; norbornadienes; stereospecificity; conformational analysis.

In a previous study of semiquinoid systems, it was found (in relation to the Rh(acac) group) that π-coordination to a transition metal sharply changes the conformation of the planar six-membered ring in 4-methyl-4-trichloromethylcyclohexa-2,5-dien-1-one (**1**) resulting in a clear-cut boat conformation of the metal complex formed (**2**)[1] (α = 35.5°, β = 21.6°, γ = 10.6°).



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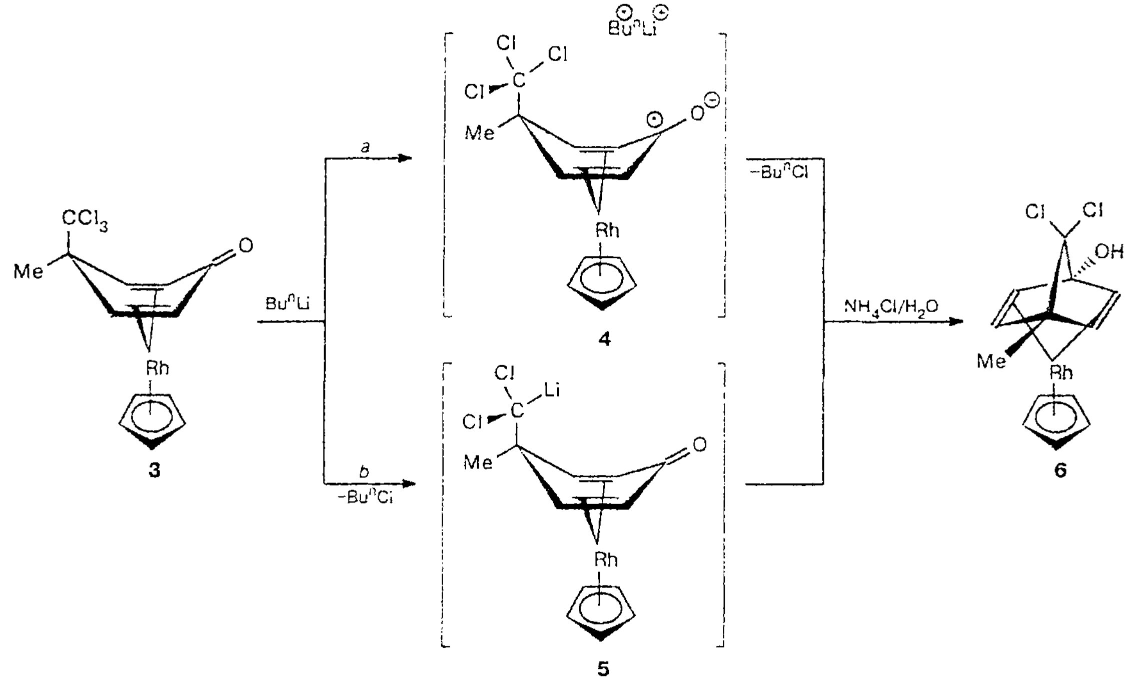
Scheme 1



In the present work, we found a promising way of using this specific conformational feature of *para*-semiquinoid organometallic compounds in fine organic synthesis.

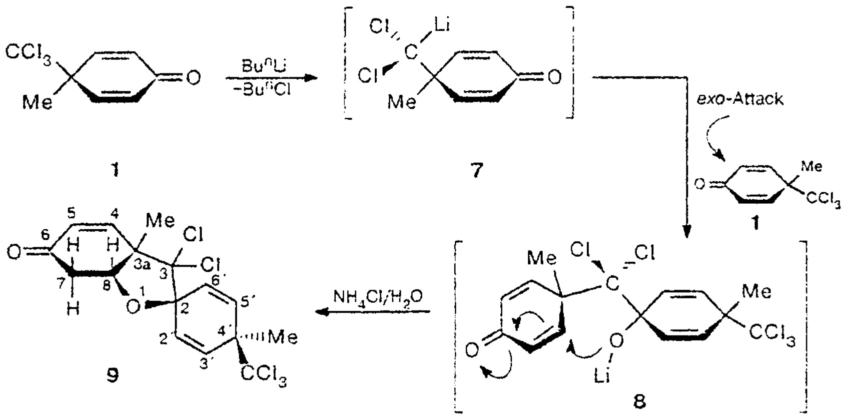
It was found (Scheme 1) that the *exo*-π-diene rhodium cyclopentadienyl complex **3**, which we prepared recently,[2] undergoes intramolecular carbocyclization in the presence of Bu^nLi in THF at −60 to −20 °C to give (η^4-7,7-dichloro-1-hydroxy-4-methylbicyclo[2.2.1]hepta-2,5-diene)(η^5-cyclopentadienyl)rhodium(I) (**6**) (yield 77%), whose structure was confirmed by elemental analysis, IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, and mass spectrometry. The discovered reaction makes it possible to develop a fundamentally novel strategy for the synthesis of bridgehead-substituted hydroxy derivatives of norbornadiene. The first step of the mechanism of this transformation may involve either single-electron reduction of the carbonyl group in the initial molecule **3** by butyllithium resulting in the generation of intermediate radical anion **4** (see Scheme 1, pathway *a*) or halogen—lithium exchange giving the unusual *gem*-dichloromethyllithium-substituted *para*-semiquinoid intermediate **5** (see Scheme 1, pathway *b*). At this point, it is the close proximity of the chemically reactive 1- and *exo*-4-groups in the above-presented boat-like conformations of the metal-coordinated reacting molecules that promotes the subsequent intramolecular closure of the second ring in the intermediates to yield compound **6**.

In order to find out whether this transformation is general and to compare its course for metal-coordinated and non-coordinated *para*-semiquinoid ligands, we carried out the reaction of Bu^nLi (Scheme 2) with free (non-coordinated) dienone **1**[3] under the same experimental conditions. X-ray diffraction data for other compounds of this class indicate that the six-membered ring in this compound should be planar.[4–6]

Chromatography of the resulting complex mixture of products on SiO_2 yielded compound **9** as the major product. According to ^1H NMR, IR, and mass spectra, this compound has a tricyclic spirofuran structure (for other examples of the formation of furanoid systems in heteroorganic transformations of *para*-semiquinoid ligands, see Refs. 7 and 8). The most characteristic features of the ^1H NMR spectrum of compound **9** proving its structure are the clearly manifested signals for all six of its olefinic protons ($^3J_{H-H} \approx 10.5$ Hz) as well as the chemical shift (4.68 ppm) and the multiplicity (ddd, $^4J_{8-4} = 2.6$ Hz, $^3J_{8-7} = 2.9$ Hz, $^3J_{8-7} = 3.16$ Hz) of the signal corresponding to the proton in position 8 of the cyclohexenone ring.

This result (see Scheme 2) confirms our hypothesis that the transformations under consideration may involve the intermediate formation of unusual *gem*-CCl_2Li-substituted *para*-semiquinoid intermediates **5** and **7**. In the latter case, intermediate **7** exists apparently in a planar conformation; therefore it is stabilized through intermolecular rather than intramolecular attack by the reactive organolithium fragment incorporated in it on the carbonyl group in the starting dienone **1** followed by the closure of a five-membered ring, which occurs *via* the attack on the activated enone fragment of the mol-

Scheme 2



ecule by an alcoholate group (8). The fact that the final product 9 is obtained as a single stereoisomer is probably due to the fact that both these elementary steps are stereospecific: first, the nucleophilic attack on the molecule of dienone 1 occurs preferably from the side opposite its CCl_3 group, (for other examples of *exo*-orientation in reactions of trichloromethyl substituted cyclohexadienes, see Refs. 1,8—10), and after that, intramolecular heterocyclization also occurs from the sterically more accessible side opposite the neighboring Me substituent.

Experimental

All reactions were carried out in an argon atmosphere; the course of the reactions was monitored by TLC on Silufol-UV-254 plates. Preparative column chromatography was performed using Silpearl UV-254 SiO_2. IR spectra were recorded on a UR-20 spectrophotometer (Carl Zeiss), and NMR spectra were obtained on a Bruker AMX-400 instrument (^{1}H, 400.13 and ^{13}C, 100.61 MHz) using tetramethylsilane as the internal standard. EI mass spectra were obtained on a MS-890 mass spectrometer (70 eV).

All solvents were thoroughly purified by standard procedures. Dienone 1[3] and its *exo*-η^4-coordinated CpRh-metal complex 3[2] were obtained by procedures described previously.

(η^4-7,7-Dichloro-1-hydroxy-4-methylbicyclo[2.2.1]hepta-2,5-diene)(η^5-cyclopentadienyl)rhodium(I) (6). Bu^{n}Li (0.25 mmol, 0.25 mL of a 1.0 *M* solution in *n*-hexane) was added with stirring at −60 °C to a solution of complex 3 (80 mg, 0.2 mmol) in 15 mL of THF. The mixture was heated to 0 °C and treated with 2 mL of a 2 *M* aqueous solution of NH_4Cl, and the organic layer was separated and concentrated. Chromatography of the residue on SiO_2 and subsequent recrystallization of the compound with R_f = 0.8 (CH_2Cl_2—Pr^{i}OH, 3 : 1) from *n*-hexane gave 55 mg of compound 6 (77%), m.p. 153—154 °C (decomp.). Found (%): C, 43.49; H, 4.04; Cl, 20.29. $C_{13}H_{13}Cl_2ORh$. Calculated (%): C, 43.48; H, 3.64; Cl, 19.75. IR (KBr), ν/cm^{-1}: 1460, 1410, 1390, 1330, 1245, 1210, 1090, 1020, 880, 810. ^{1}H NMR ($CDCl_3$), δ: 1.24 (s, 3 H, Me); 2.48 (br.s, 1 H, OH); 3.02 (dd, 2 H, 2 CH, $^2J_{H-H}$ = 3.8 Hz, $^2J_{H-Rh}$ = 2.7 Hz); 3.28 (dd, 2 H, $^3J_{H-H}$ = 3.8 Hz, $^2J_{H-Rh}$ = 2.8 Hz); 5.29 (d, 5 H, Cp, $^2J_{H-Rh}$ = 0.8 Hz). ^{13}C NMR {^{1}H} ($CDCl_3$), δ: 11.42 (s, Me); 30.93 (d, 2 CH, $^1J_{C-Rh}$ = 9.8 Hz); 32.44 (d, 2 CH, $^1J_{H-Rh}$ = 10.1 Hz); 61.17 (s, <u>C</u>—Me); 85.33 (s, Cp); 93.42 (s, C—OH); 111.29 (s, CCl_2). MS (EI), *m/z* (I_{rel} (%)): 358 [M]$^+$ (7.7), 343 [M−Me]$^+$ (8.7), 322 [M−HC]$^+$ (76.3), 287 [M−HCl−Cl]$^+$ (69.7), 103 [CpRhCl]$^+$ (76.1), 168 [CpRh]$^+$ (91.9), 155 [M−CpRhCl]$^+$ (100).

3,3-Dichloro-3a,4′-dimethyl-4′-trichloromethyl-2,3,3a,6,7,8-hexahydrospiro[benzofuran-2,1′-cyclohexa-2′,5′-dien]-6-one (9). Bu^{n}Li (0.80 mmol, 0.37 mL of a 2.17 *M* solution in *n*-hexane) was added with stirring at −60 °C to a solution of dienone 1 (150 mg, 0.67 mmol) in 15 mL of THF. The mixture was heated to 0 °C and treated with 2 mL of a 2 *M* aqueous solution of NH_4Cl, and the organic layer was separated and concentrated. Chromatography of the residue on SiO_2 followed by recrystallization of the compound with R_f = 0.5 (toluene—Et_2O, 4 : 1) from Et_2O gave 33 mg of product **9** (24%). IR (KBr), ν/cm^{-1}: 3000 (C—H); 1700 (C=O); 1460, 1415, 1300, 1245, 1195, 1135, 1080, 1025, 990, 800. ^{1}H NMR ($CDCl_3$), δ: 1.51 (s, 3 H, Me); 1.56 (s, 3 H, Me); 2.59 (dd, 1 H, H-7, $^2J_{7-7}$ = 17.9 Hz, $^3J_{7-8}$ = 2.9 Hz); 2.92 (dd, 1 H, H-7, $^2J_{7-7}$ = 17.9 Hz, $^3J_{7-8}$ = 2.9 Hz); 4.68 (ddd, 1 H, H-8, $^4J_{8-4}$ = 2.6 Hz, $^3J_{8-7}$ = 2.9 Hz, $^3J_{8-7}$ = 3.16 Hz); 5.92 (dd, 1 H, CH, $^3J_{H-H}$ = 10.57 Hz, $^4J_{H-H}$ = 2.53 Hz); 6.15 (d, 1 H, H-5, $^3J_{4-5}$ = 10.48 Hz); 6.24 (dd, 1 H, CH, $^3J_{H-H}$ = 10.48 Hz, $^4J_{H-H}$ = 2.53 Hz); 6.26 (dd, 1 H, CH, $^3J_{H-H}$ = 10.57 Hz, $^4J_{H-H}$ = 2.63 Hz); 6.46 (dd, 1 H, H-4, $^3J_{H-H}$ = 10.48 Hz, $^4J_{H-H}$ = 2.62 Hz). MS (EI), *m/z* (I_{rel} (%)): 379 [M−Cl]$^+$ (2.4), 308 [M−2 Cl−HCl]$^+$ (4.5), 293 [M−2 Cl−HCl−Me]$^+$ (4.0), 227 [M−CCl_3−2 Cl]$^+$ (6.1), 193 (33.4), 155 (64.0), 127 (77.0).

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