

γ -Lithioalkoxides as Convenient Reagents for the Synthesis of Pentacarbonyl(2-oxacyclopentylidene)chromium Complexes

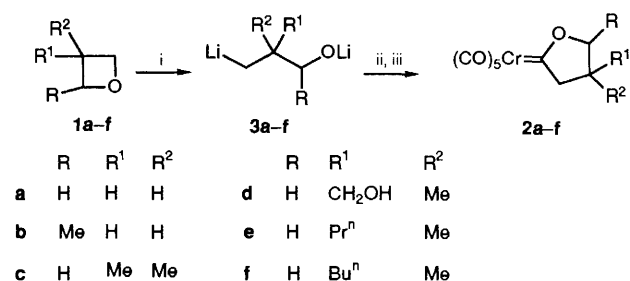
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 γ -Lithioalkoxides generated by reductive lithiation of oxetanes **1a–f** are employed in the synthesis of pentacarbonyl(2-oxacyclopentylidene)chromium complexes **2a–f**.

Aromatic radical-anions generate carbanions from halides,¹ phenyl alkyl sulfides,² oxiranes,³ oxetanes⁴ and tetrahydrofurans,⁵ which are potentially useful in the synthesis of Fischer-type chromium carbene complexes. In particular Cohen showed that γ -lithioalkoxides can be efficiently generated by reductive lithiation of readily available oxetanes using lithium 4,4'-di-*tert*-butylbiphenylide (LDBB).⁴

We report here that γ -lithioalkoxides **3a–f**, generated by LDBB from the oxetanes **1a–f**, can be employed as organolithium reagents in the synthesis of pentacarbonyl(2-oxacyclopentylidene)chromium complexes.⁶ The tetrahydrofuran (THF) solution of γ -lithioalkoxides **3a–f**, produced by adding oxetanes **1a–f** (1 mmol) to a solution of LDBB (2 mmol) generated from 2 mmol of DBB and 2.2 mmol of lithium in 5 ml of THF at 0 °C, is added by a cannula to a solution of Cr(CO)₆ (1 mmol) in THF (10 ml). The reaction mixture is quenched with 20 ml of water, then Me₃O⁺BF₄⁻ (2 mmol) is added. The reaction products **2a–f** are extracted with diethyl ether and purified by flash column chromatography (Scheme 1).



Scheme 1 Reagents and conditions: i, LDBB, THF, 0 °C, 1 h; ii, Cr(CO)₆, THF, room temp., 15 min; iii, Me₃O⁺BF₄⁻

Table 1 Pentacarbonyl(2-oxacyclopentylidene)chromium complexes **2a–f** synthesized

Product ^a	M.p./°C (solvent)	Yield(%)
2a	63 (pentane, -78 °C)	17
2b	Oil	14
2c	56 (pentane, -78 °C)	53
2d	46 (CH ₂ Cl ₂ -hexane)	41
2e	Oil	29
2f	Oil	27

^a All new compounds gave satisfactory elemental analyses

As expected, the reduction of the 2-substituted oxetane **1b**, gives the less substituted carbanion **3b**, and, in this case, the 5-unsubstituted derivative **2b** is obtained. In addition the best yields are achieved starting from the 3,3-disubstituted oxetanes **3c–f** (Table 1).[†]

Yields probably reflect a compromise between the rate of oxetane reduction with LDBB and the stability of corresponding γ -lithioalkoxide. In fact, as reported,⁴ 3,3-disubstituted oxetanes undergo a slower reduction but give also the most stable γ -lithioalkoxides.

3,3-Disubstituted oxetanes **1c–f**, which are not commercially available, have been synthesized by reduction of the 2,2-dialkyl malonates with LiAlH₄ to give the corresponding 1,3-diols.⁷ These are converted into oxetanes following standard literature procedures.⁸

At the moment this method represents the best way to synthesize 4,4-disubstituted pentacarbonyl(2-oxacyclopentyl-

[†] All new compounds gave satisfactory elemental analyses; **2a–b** were known compounds.⁹ *Spectral data* for the new compounds: **2c** IR (Nujol): $\nu_{\max}/\text{cm}^{-1}$ 2064, 2000–1800 (v CO); ¹H NMR (CDCl₃, 80 MHz): δ 1.10 (s, 6H, -CH₃), 3.42 (s, 2H, -CH₂-C=Cr), 4.53 (s, 2H, -OCH₂-); ¹³C NMR (CDCl₃, 200 MHz): δ 24.89 (-CH₃), 37.23 [-C(CH₃)₂], 74.96 (-CH₂-C=Cr), 94.78 (-CH₂-O-), 216.16 (CO *cis*), 223.53 (CO *trans*), 346.40 (-C=Cr); *m/z*: 290 (M⁺); **2d** IR (Nujol): $\nu_{\max}/\text{cm}^{-1}$ 3312 (v OH), 2064, 2000–1876 (v CO); ¹H NMR (CDCl₃, 80 MHz): δ 1.09 (s, 3H, -CH₃), 1.66 (br s, 1H, OH), 3.26 (d, 1H, *J*_{gem} 20.5 Hz, =C-CH-), 3.44 (s, 2H, -CH₂-OH), 3.66 (d, 1H, *J*_{gem} 20.5 Hz, =C-CH-), 4.51 (d, 1H, *J*_{gem} 9.4 Hz, -O-CH-), 4.86 (d, 1H, *J*_{gem} 9.4 Hz, -O-CH-); ¹³C NMR (CDCl₃, 300 MHz): δ 20.30 (-CH₃), 42.27 [-C(CH₃)CH₂OH], 67.02 (=C-CH₂-), 70.43 (-CH₂OH), 91.70 (-O-CH₂-), 216.25 (CO *trans*), 223.55 (CO *cis*); *m/z*: 306 (M⁺); **2e** IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 2073, 2000–1870 (v CO); ¹H NMR (CDCl₃, 80 MHz): δ 0.93 (t, 3H, *J*_{vic} 6.7 Hz, -CH₃), 1.03 (s, 3H, -CH₃), 1.12–1.42 (m, 4H, -CH₂-CH₂-), 3.31 (d, 1H, *J*_{gem} 19.4 Hz, =C-CH-), 3.44 (d, 1H, *J*_{gem} 19.4 Hz, =C-CH-), 4.51 (d, 1H, *J*_{gem} 9.7 Hz, -O-CH-), 4.58 (d, 1H, *J*_{gem} 9.7 Hz, -O-CH-); ¹³C NMR (CDCl₃, 200 MHz): δ 13.77 (-CH₂-CH₃), 23.11 (-C-CH₃), 27.40 (-CH₂-CH₃), 38.29 (-CH₂-CH₂-CH₃), 40.48 [-C(CH₃)-Prⁿ], 73.60 (=C-CH₂-), 94.03 (-O-CH₂-), 216.24 (CO *trans*), 223.48 (CO *cis*), 345.61 (Cr=C-); *m/z*: 318 (M⁺); **2f** IR (neat): $\nu_{\max}/\text{cm}^{-1}$ 2064, 2000–1890 (v CO); ¹H NMR (CDCl₃, 80 MHz): δ 0.88 (t, 3H, *J*_{vic} 7 Hz, -CH₃), 1.03 (s, 3H, -CH₃), 0.93–1.52 [m, 6H, -(CH₂)₃-], 3.32 (d, 1H, *J*_{gem} 19.5 Hz, =C-CH-), 3.43 (d, 1H, *J*_{gem} 19.5 Hz, =C-CH-), 4.51 (d, 1H, *J*_{gem} 9.5 Hz, -O-CH-), 4.58 (d, 1H, *J*_{gem} 9.5 Hz, -O-CH-); ¹³C NMR (CDCl₃, 200 MHz): δ 14.41 (-CH₂-CH₃), 18.50 (-CH₂-CH₃), 23.04 (-CH₂-CH₂-CH₂-CH₃ + -C-CH₃), 40.54 [-C(CH₃)-Buⁿ], 40.78 [-CH₂-(CH₂)₂-CH₃], 76.63 (=C-CH₂-), 94.05 (-O-CH₂-), 216.51 (CO *trans*), 223.51 (CO *cis*), 345.59 (Cr=C-); *m/z*: 322 (M⁺).

idene)chromium carbene complexes. In fact, methods reported in the literature⁹ including our procedure, which is of rather general applicability, do not allow the synthesis of such derivatives. Particularly, the present procedure has given us access to the 4,4-dimethyl-2-oxacyclopentylidenechromium carbene complex **2c**, that we have employed in elucidating the mechanism of the reaction of pentacarbonyl(2-oxacyclopentylidene)chromium carbene complexes with the dialkylacetals of dimethylformamide.¹⁰

Work is in progress to evaluate the potential of aromatic radical-anions to produce carbanion species suitable for the synthesis of pentacarbonylchromium carbene complexes.

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