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Preliminary communication

REACTIONS OF CONJUGATE BASES OF METAL CARBENE COMPLEXES WITH EPOXIDES AND WITH α-BROMO ESTERS

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Summary

The reactions of the conjugate base of (methylmethoxycarbene)pentacarbonylchromium(0) with epoxides and with methyl bromoacetate give alkylated carbene complexes which cannot be obtained by previous synthetic routes.

The usual preparative route to transition metal—carbene complexes (for recent reviews see ref. 1) involves the attack of an organolithium reagent on a coordinated carbonyl group to give an anionic acyl complex which can then be alkylated on oxygen with strongly electrophilic reagents such as trimethyloxonium fluoroborate or methyl fluorosulfonate [2]. This synthetic method is limited by the availability of organolithium reagents: only functional groups which are compatible with lithium reagents may be introduced into the carbene complex by such routes. Recently, we described the generation and some reactions of carbanions α to the carbene carbon atom of transition metal complexes [3, 4]. Here we report the reaction of these "carbene anions" with epoxides and with bromoesters which provide complexes which cannot be prepared directly from lithium reagents and metal carbonyl compounds.

The conjugate base of $(CO)_5CrC(OCH_3)CH_3$ (Ia) may be conveniently generated by treatment with n-butyllithium**. Treatment of this anion with ethylene oxide gives (2-oxacyclopentylidene)pentacarbonylchromium(0) (IIa) in 50% yield***. The reaction can be envisioned as a nucleophilic attack of the carbene anion on the epoxide followed by intramolecular displacement of methoxide from the intermediate adduct.

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[**] Much weaker bases may also be employed since Ia is one of the most acidic neutral carbon acids known [4].

[***] Previously oxacyclopentylidene complexes have been prepared by novel procedures involving either the reaction of metal carbonyl anions with 1,3-dibromopropane [5, 6] or the reaction of acetylenic alcohols with platinum complexes [7].

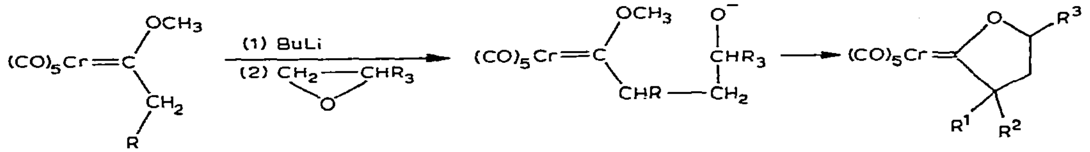
TABLE 1

SPECTRAL CHARACTERIZATION OF METAL—CARBENE COMPLEXES

Compound	M.p. (°C)	NMR[a]	IR[b]
IIa	63—65	4.90 (t, J 8Hz, 2H), 3.67 (t, J 8Hz, 2H) 1.96 (quintet, J 8Hz, 2H)	2066 s, 1983 m, 1958 s, 1944 s[c]
IIb	oil	5.13 (m, 1H), 4.2—3.0 (m, 2H, AB portion of ABXY system, δ_A 3.85, δ_B 3.42, J_{AB} 19.5, $J_{AX} = J_{BY} = J_{BX} = 9$, J_{AY} 5), 1.58 (d, J 7Hz, 3H), 2.4—1.0 (m, 2H)	2060 s, 1990 m, 1960 s, 1940 vs
IIc	28—29	4.85 (t, J 7Hz, 2H), 3.60 (m, 1H), 1.42 (d, J 7Hz, 3H), 2.4—1.2 (m, 2H)[e]	2062 m, 1985 m, 1952 s, 1938 s
IId	61—62.5	5.04 (t, J 7Hz, 2H), 1.87 (t, J 7Hz, 2H), 1.48 (s, 6H)	2067 s, 1982 m, 1950 s, 1943 s, 1925 s[c]
IIe	70—72	4.85 (t, J 7Hz, 2H), 3.74 (t, J 7Hz, 2H), 2.6—1.6 (m, 5H), 1.38 (s, 3H)[d,e]	2060 m, 1985 m, 1955 vs, 1935 vs[c]
III	oil	4.77 (s, 3H), 3.5—3.7 (m, 5H)[f], 2.44 (t, J 7Hz, 2H)	2065 s, 1985 m, 1945 vs, 1740 s
IV	oil	4.88 (s, 3H), 4.70 (m, J 8Hz, 1H), 3.68 (s, 6H), 2.61 (dd, J 7Hz, J' 17Hz, 2H), 2.29 (dd, J 7Hz, J' 17 Hz, 2H)	2065 s, 1985 m, 1945 vs, 1740 s

[a] δ values; recorded at 100 MHz in CS_2. [b] Frequency in cm^{-1}; measured in CS_2. [c] Measured in heptane. [d] Measured in $CDCl_3$. [e] 60 MHz spectrum. [f] Becomes a triplet (2H, J 7, δ 2.74) and singlet (3H, δ 2.24) with 20 mole% $Pr(fod)_3$, CCl_4 (fod = heptafluorodimethyloctanedionate).

The carbene anion of Ia attacks propylene oxide at the least hindered carbon atom to give the 3-methylcyclopentylidene complex IIb in 38% yield.



(Ia) R = H
(Ib) R = CH_3

(IIa) R^1, R^2, R^3=H
(IIb) R^1, R^2=H; R^3= CH_3
(IIc) R^1 = CH_3; R^2, R^3= H
(IId) R^1, R^2=CH_3; R^3=H
(IIe) R^1= CH_3, R^2= CH_2CH_2OH, R^3= H

The 5-methylcyclopentyilidene complex IIc can be obtained in 18% yield from the reaction of the anion of the ethylmethoxycarbene complex Ib with ethylene oxide; in addition, the reaction gave a 42% yield of IIe, the product of the subsequent reaction of the conjugate base of IIc with ethylene oxide*. We have also observed dialkylation in the methylation of IIa with one equivalent of n-butyllithium followed by one equivalent of methyl fluorosulfonate; the reaction mixture contains monomethylated carbene complex IIc, dimethylated carbene complex IId, and the unmethylated starting material IIa in a ratio of 2.4/1.9/1.0.

The reaction of the carbene anion of Ia with one equivalent of methyl bromoacetate gave 37% monoalkylation product III and 20% dialkylation product IV.

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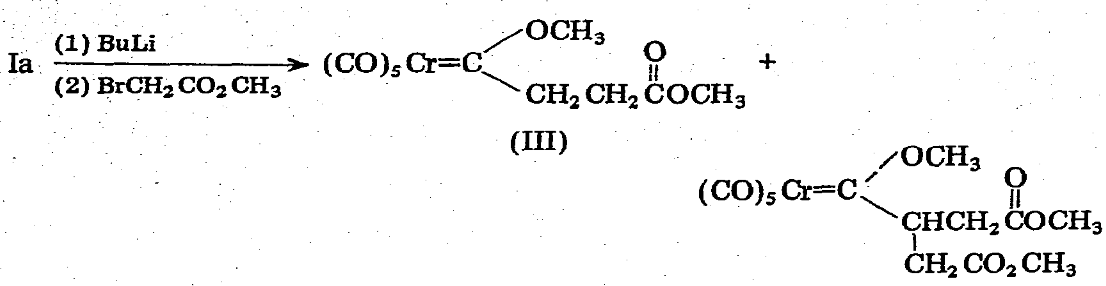
*None of the analogous dialkylation product was found in the preparation of IIa.



(III)

(IV)

The spectral properties of the compounds are listed in Table 1*.

The preparation of IIa illustrates the experimental procedure. n-Butyllithium (20.0 ml, 2.06 *M*, 41.2 mmol) was added to Ia (10.0 g, 40.0 mmol) in 250 ml diethyl ether at —78° to give a pale yellow solution of the carbene anion. The solution was warmed to 0° and ethylene oxide (3 ml, 61.2 mmol) was added. After 30 minutes at 0°, the reaction mixture was quenched with water. Column chromatography (silica gel, pentane) gave 1.5 g recovered Ia and the oxacyclopentylidene complex IIa (4.4 g, 50%).

The structural elaboration of carbene complexes via reactions of carbene anions complements the increasing variety of transformations of carbene complexes into organic compounds. Fischer has reported the synthesis of cyclopropanes from the reaction of metal carbene complexes with α,β-unsaturated esters and with vinyl ethers [8]. We have recently reported the synthesis of vinyl ethers from the reaction of metal carbene complexes with diazoalkanes [9] or with Wittig reagents [10] and the synthesis of esters from the oxidation of carbene complexes [10]. The continued development of means of elaborating simple carbene complexes and of means of releasing the carbene ligand from its metal complex should make metal—carbene complexes useful synthetic reagents.

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[*] The elemental composition of all new compounds was determined by measurement of the exact mass of the molecular ion in the high resolution mass spectrum. All new compounds were homogeneous on thin layer chromatography (silica gel, hexane).