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Reductive Olefination of Aldehydes via Chromium-Brook Rearrangement

Rachid Baati[†], Charles Mioskowski[†], Deb Barma[‡], Rajashaker Kache[‡], and J. R. Falck[‡]

[†]Laboratoire de Synthèse Bio-Organique, UMR 7175/LC1-CNRS, Faculté de Pharmacie, Université Louis Pasteur de Strasbourg, 74 Route du Rhin, BP 60024, 67 401 Illkirch, France

[‡]Department of Biochemistry, University of Texas Southwestern Medical Center, Dallas, Texas 75390 USA

Abstract

The combination of CrCl₂ and silyl chlorides converts aryl and conjugated aldehydes into olefinic adducts in good to excellent yields. When constrained by structural features, the intermediate *vic*-diol can be isolated. Available data are consistent with a novel chromium-Brook rearrangement.

The inter- and intramolecular reductive coupling of carbonyls to generate olefins is popularly known as the McMurry reaction.¹ It is most often conducted using low-valent titanium, although other metals have been utilized.² Mechanistically, the carbonyl forms a transient ketyl that dimerizes on or near the metal surface.³ The resultant metalpinacolate undergoes stepwise cleavage of the C-O bonds resulting in formation of an alkene. Carbenoid intermediates may also be involved depending upon reaction conditions and/or structural features.⁴ The geometry of the newly formed double bond is controlled principally by thermodynamic factors. Comparable reductions of carbonyls by chromium(II), on the other hand, typically lead to pinacols.⁵ In contrast, we have observed that the combination of CrCl₂ and silyl chlorides generally converts aryl and conjugated aldehydes into olefinic adducts in good to excellent yields.⁶ Consequently, we initiated a study to define the scope of the reaction and mechanistic *raison d'être* for the differences in outcomes.

The olefination was optimized using benzaldehyde (**1**) which furnished *trans*-stilbene (**2**) (Table 1).⁷ The best yield and fastest reaction time were obtained with trichlorosilane and CrCl₂ in THF at reflux (entry 1). EtOAc was also satisfactory (entry 2), whereas THF/DMF (1:1) generated *threo*-dihydrobenzoin (58%) and benzyl alcohol (36%) only.⁸ Repetition of the reaction described in entry 1, but utilizing catalytic CrCl₂ (10 mol %) regenerated by Mn⁹ (4 equiv), also led to a mixture of *threo*-dihydrobenzoin and benzyl alcohol. Control experiments confirmed both trichlorosilane and CrCl₂ were necessary for olefin formation.

A variety of other chlorosilanes in THF likewise afforded olefinated adducts, *inter alia*, methyl trichlorosilane (entry 3), ethyl trichlorosilane (entry 4), phenyl trichlorosilane (entry 5), dimethyl dichlorosilane (Entries 6 and 7), trimethyl chlorosilane (entry 8), and 1,3-dichloro-1,1,3,3-tetraisopropylidisiloxane (entry 9). The outcomes of these reactions broadly followed the overall reactivity of the chlorosilanes toward chromium.

Aldehydes bearing an electron withdrawing substituent (**3**, entry 10),^{10,11} electron donating group (**5**, entry 11),¹² and fused aromatic (**7**, entry 12)¹³ gave generally similar results.

Mioskow@aspirine.u-strasbg.fr

j.falck@utsouthwestern.edu

Importantly, many functional groups were well tolerated, e.g., bromide (**9**, entry 13),¹⁴ methylenedioxy (**11**, entry 14),^{15,16} benzyl/methyl ethers (**13**, entry 15),¹⁷ and, surprisingly, an unprotected phenol (**15**, entry 16).¹⁸ The conjugated aldehyde cinnamaldehyde (**17**) was also well behaved and led to triene **18** (entry 17).¹⁹ However, aliphatic aldehydes and unhindered ketones principally afforded aldol products under the same reaction conditions. The intramolecular condensation of dialdehyde **19** gave rise unexpectedly to *trans*-diol **20** (entry 18),²⁰ presumably because it could not close to form the cyclic chromium-diester necessary for elimination (*vide infra*).

While the details must be confirmed, we favor a mechanism whereby the silyl anion, formed via successive one electron transfers from Cr(II),²¹ adds to the aldehyde to give α -hydroxysilane **21** which undergoes chromium-Brook rearrangement to organochromium **22** (Figure 1). Numerous other metals and non-metals are known to undergo similar transformations.²² Subsequent addition of **22** to a second equivalent of aldehyde furnishes pinacol **23**. The isolation of *trans*-diol **20** as the sole product in entry 18 suggests cyclic chromate ester **24**, which cannot form in this case, is the obligate intermediate for elimination to olefin **25**. As would be anticipated from this mechanistic hypothesis, heating the aldehyde and CrCl₂ or silyl chloride together for several hours prior to addition of the remaining ingredients does not yield olefinic adducts. But, good yields of adduct are obtained when the silyl chloride and CrCl₂ are heated together for several hours followed by addition of the aldehyde.

These data reveal a novel entry into an otherwise unattainable class of functionalized-chromium anions. Efforts to exploit them as reagents for organic synthesis will be detailed elsewhere.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Proposed chromium-Brook rearrangement.

Table 1Reductive Olefination of Aldehydes using $\text{CrCl}_2/\text{Silyl Chlorides}$

entry	aldehyde	olefin	silane	solvent temp (°C)/ time (h)	yield(%)
1			HSiCl_3	THF, 67/8	95
2			HSiCl_3	EtOAc , 76/14	82
3			MeSiCl_3	THF, 65/24	72
4			EtSiCl_3	THF, 65/24	65
5			PhSiCl_3	THF, 65/24	68
6			Me_2SiCl_2	THF, 65/12	76
7			Me_2SiCl_2	EtOAc , 76/12	74
8			Me_3SiCl	THF, 65/12	62
9			$[(\text{tPr})_2\text{ClSiO}]_2$	THF, 65/12	45
10			HSiCl_3	THF, 65/12	74 ^d
11			HSiCl_3	THF, 65/8	87
12			HSiCl_3	THF, 65/8	90
13			HSiCl_3	THF, 65/12	65
14			HSiCl_3	THF, 65/8	84 ^b

entry	aldehyde	olefin	silane	solvent temp (°C)/ time (h)	yield(%)
15			HSiCl ₃	THF, 65/8	92
16			HSiCl ₃	THF, 65/8	82
17			HSiCl ₃	THF, 65/8	83
18			HSiCl ₃	THF, 65/12	95

^a 8:92 *cis/trans* by GC analysis.

^b 35:65 *cis/trans* by GC analysis.