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RESEARCH ARTICLE

SYNTHESES OF NOVEL α,β -UNSATURATED CHROMIUM FISCHER CARBENE COMPLEXES USING β -BROMOSTYRENE

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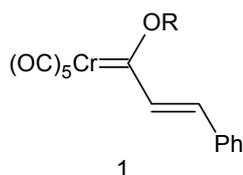
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ABSTRACT

Syntheses of α,β -unsaturated neutral Chromium Fischer carbene complexes bearing alkoxy groups as donor substituents have been explored. Treating β -bromostyrene with a base and chromium hexacarbonyl followed by alkylation with an alkyl iodide produced the alkoxy styryl carbene complex 1 in modest yield. The results however did not show significant variation in the yield of 1 with the size of the side chain R. Owing to their resemblance to α,β -unsaturated carbonyl compounds, these compounds can provide very useful protocols for the synthesis of organic compounds.

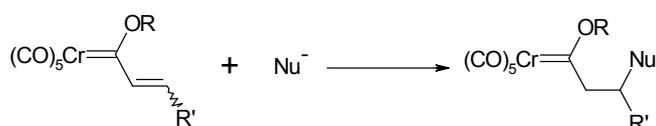


- 1a. R = isopropyl (42.0%)
1b. R = isobutyl (40.0%)
1c. R = sec-butyl (45.3%)
1d. R = benzyl (41.2%)

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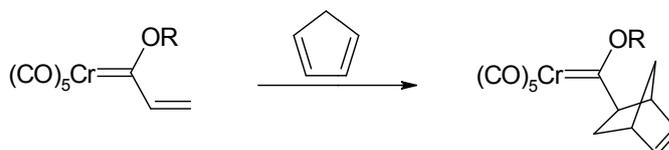
INTRODUCTION

Recent years have witnessed many developments in the synthesis and transformations of Fischer carbenes. α,β -Unsaturated chromium Fischer carbene complexes have become important reagents in synthetic organic chemistry (Frank *et al.*, 1993). Pentacarbonyl (alkenylalkoxy carbene) chromium (0) complexes fall within this class of carbene complexes. The chemistry of these carbene complexes is analogous to those of α,β -unsaturated carbonyl compounds and acid derivatives. The reactivity of these carbene complexes towards a variety of substrates has previously been reported. Nucleophilic additions to these carbenes via Michael-type additions have been studied extensively. (Nakaruma *et al.*, 1993). (Scheme 1.)



Scheme 1

[4 + 2] cycloaddition of dienes to the carbene fragment in these complexes have also been reported. (Wulff *et al.*, 1990, 1992). (Scheme 2.)



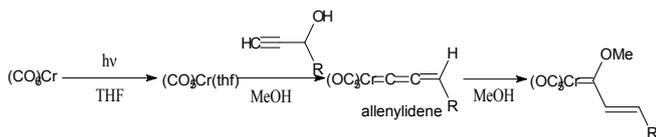
Scheme 2

A number of synthetic routes for the syntheses of α,β -Unsaturated Fischer carbenes have been developed and reported. The most common means to synthesize this class of carbene complexes is from the metal hexacarbonyl, $M(CO)_n$.

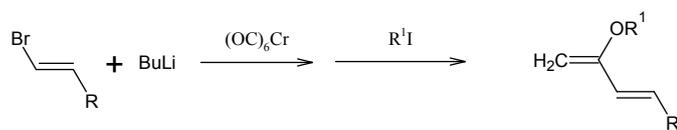
Typical examples of reported syntheses are

- Preparation via allenylidene intermediate. (Barluenga, 2006) (Scheme 3)
- Preparation from reaction of metal hexacarbonyl with vinyl bromide in the presence of a strong base, followed by alkylation. (Sultemeyer, J and Dotz, K.H., 2000) (Scheme 4).

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Scheme 3



Scheme 4

The present study was aimed at synthesizing a wide range of novel α,β -unsaturated Fischer carbenes bearing bulky alkoxy donor groups via scheme 4 due to the flexibility of alkylation. These compounds can be very useful in the development of a wide range of synthetic protocols for complex organic molecules.

EXPERIMENTAL

Materials and instrumentation

All common reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Distilled water was deoxygenated by purging with argon prior to use. β -bromostyrene was obtained as the (cis+trans) – β -bromostyrene (85:15) and used without further purification. Lithium bis(trimethylsilyl) amide was obtained as the commercially available 1.0M in THF. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Solvents for chromatography were not distilled prior to use and the silica gel used in the purification process was not deactivated before use. TLC was performed on aluminium-backed plates coated with silica gel 60. The chromatograms were visualised under ultra-violet light. All reported yields are calculated from purified compounds unless otherwise stated. NMR spectra were recorded on (Joel JNM-EX400). Chemical shifts δ for ^1H are referenced to residual chloroform (CDCl_3 , $\delta = 7.24$ ppm) as internal standard unless otherwise stated.

General synthetic procedures and reactions

All reactions involving air-sensitive compounds were carried out under argon atmosphere. Unless otherwise stated, inert atmosphere was maintained with argon filled balloon. Preparation of the carbene complexes were according to the procedure earlier reported by (Sultemeyer and Dotz, 2000) with little modification.

General synthesis of carbene complexes 10b, 10c, 10d, and 10e

Pentacarbonyl (alkoxystyryl carbene) chromium (0) complexes 10b, 10c and 10d and 10e were prepared using a similar procedure. (Scheme 4). About 9.2mmol of trans- β -bromostyrene was dissolved in 200mL dry ether in a 250mL three-neck round bottom flask at -78°C . Then about 20.2mmol (13.5mL) of t-butyllithium (1.5M in hexane) was transferred into flask via a syringe and the mixture stirred at this temperature for 2hours by which period the mixture changed from orange to deep red. About 9.2mmol (2g) $(\text{CO})_6\text{Cr}$ was then added to the deep red resulting solution obtained above and stirring prolonged for another 2hours at reflux

temperature. Solvent was removed on a rotary evaporator to obtain a red residue. The residue was dissolved in an aqueous solution of tetramethylammonium bromide (0.9g in 100mL water) and 13.8mmol of the appropriated alkyl iodide RI, added and stirring allowed for 2hours at 70°C . The resulting solution was extracted with three 30mL- portions of hexane. The combined hexane layers was dried over anhydrous magnesium sulphate and filtered through a bed of celite. Solvent was removed from filtrate and a red solid obtained.

Synthesis of pentacarbonyl(isopropoxyxyryl carbene)chromium(0), 1a.

Using isopropyl iodide as the alkylating agent in the above procedure gave carbene complex 1a (42% yield). ^1H NMR (CDCl_3): δ 7.4-7.2(m, Ar-H), 7.05(d, $\text{HC}=\text{CHPh}$), 6.7(d, $\text{HC}=\text{CHPh}$), 4.34(m, $\text{HC}(\text{CH}_3)_2$), 1.8(d, $(\text{CH}_3)_2$). Rf = 0.63 (hexanes).

Synthesis of pentacarbonyl(sec-butyloxyxyryl carbene)chromium(0), 1b.

Using sec-butyl iodide as the alkylating agent gave carbene complex 1b (40% yield). ^1H NMR (CDCl_3): δ 7.4-7.2(m, Ar-H), 7.02(d, $\text{HC}=\text{CHPh}$), 6.7(d, $\text{CH}=\text{CHPh}$), 4.0(m, HC), 1.8(m, $\text{HC}-\text{CH}_2$), 1.6(d, $\text{HC}-\text{CH}_3$), 1.0(t, CH_2CH_3). Rf = 0.47 (hexanes)

Synthesis of pentacarbonyl (isobutyloxyxyryl carbene)chromium (0), 1c.

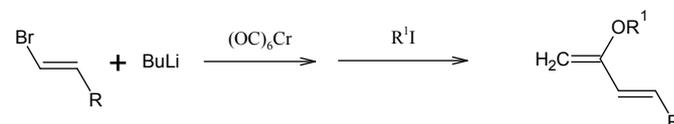
Using isobutyl iodide as the alkylating agent gave carbene complex 1c (45.3% yield). ^1H NMR (CDCl_3): δ 7.6-7.3(m, Ar-H), 3.4(d, OCH_2), 2.0(m, CH), 1.1(d, CH_3). Rf = 0.33(hexanes)

Synthesis of pentacarbonyl (benzyloxyxyryl carbene)chromium(0), 1d.

Using benzyl iodide as the alkylating agent gave carbene complex 1d (41.2% yield). ^1H NMR (CDCl_3): δ 7.6-7.2(m, Ar-H), 7.1(d, $\text{HC}=\text{CHPh}$), 4.6(s, CH_2). Rf = 0.49 (hexanes).

RESULTS AND DISCUSSION

We adopted the procedure reported in scheme 4 for syntheses of 1a,b,c,d using β -bromostyrene.



Entry	R ¹	1 (yield)
1	isopropyl	1a (43%)
2	sec-butyl	1b (40%)
3	isobutyl	1c (45.3%)
4	benzyl	1d (41.2%)

CONCLUSION

We were able to synthesize four novel α,β -unsaturated Fischer carbene complexes by treating β -bromostyrene with

butyllithium followed by chromium hexacarbonyl and alkylating with a range of alkyl iodides.

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