

Efficient synthesis of 2-alkoxy-1,3-butadienes by methylenation of alkenyl Fischer carbene complexes

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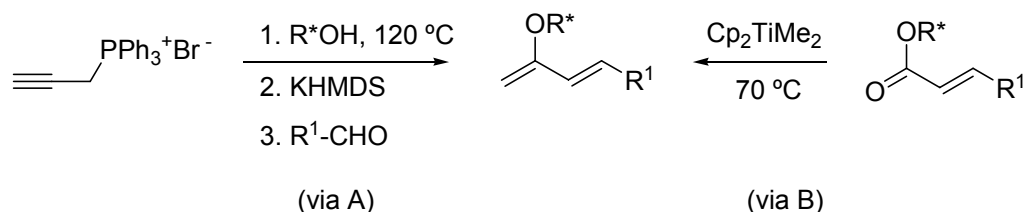
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Abstract. The thermal reaction of chromium alkenyl carbene complexes **1** and 1,1-dimethylpropadiene **2** results in the efficient formation of achiral and chiral 2-alkoxy-1,3-butadienes **4**. This process represents a new protocol for the methylenation of α,β -unsaturated Fischer carbene complexes.

Keywords: Fischer carbene complexes, methylenation, 2-alkoxy-1,3-butadiene synthesis

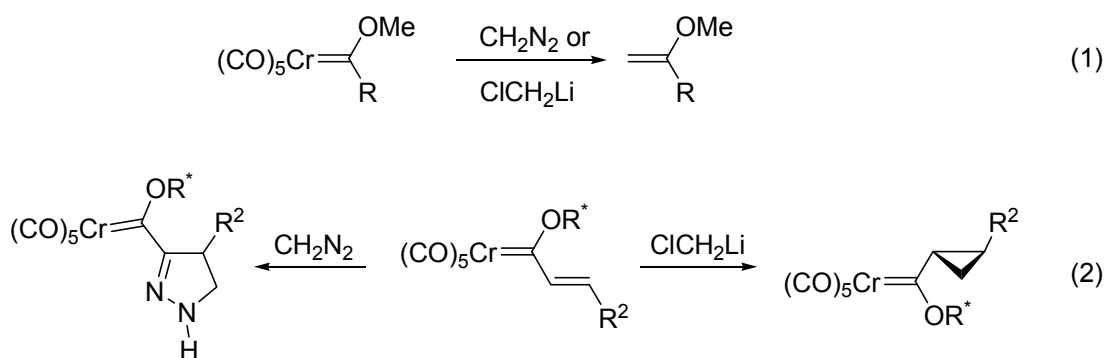
Introduction

Heterosubstituted 1,3-butadienes have found numerous applications in the synthesis of functionalized cyclohexene derivatives by cycloaddition reactions.¹ While a number of methodologies for the synthesis of achiral and, to a much lesser extent, chiral 2-amino-1,3-butadienes have been reported,² the corresponding 2-alkoxy-1,3-butadienes have been scarcely investigated, probably due to the difficulties associated with their preparation. While classical routes appear rather toilsome to access common 2-alkoxy-1,3-butadienes, sometimes they become unsuitable for derivatives with higher structural complexity, particularly chiral 2-alkoxy-1,3-dienes.³ Thus, we found that these systems could be synthesized in moderate yields in two ways (Scheme 1): i) reaction of propargylphosphonium salts with chiral alcohols followed by the Wittig olefination (Route A), and ii) methylenation of carboxylic acid derivatives with dimethyltitanocene (Petasis reagent) (Route B).⁴



Scheme 1. Reported approaches for the synthesis of chiral 2-alkoxydienes.

Although, the methylenation reaction represents a straightforward entry into such dienes, the problems associated with the titanium-based reagent prompted us to design a more efficient methylenation reaction. Since carbene-type substrates are well known to readily undergo methylenation, we focused our attention onto transition-metal alkoxy-carbene complexes (Fischer carbene complexes) as more appropriate precursor systems of alkoxydienes. Their attractiveness seems obvious in terms of stability, availability in multigram scale, and reactivity.⁵ In this context, the rapid methylenation of simple carbene complexes has been reported with diazomethane⁶ and chloromethylithium⁷ (Scheme 2, eq. 1). On the contrary, severe problems arise when the methylenation reaction is extended to alkenyl carbene complexes, being the conjugate addition the major drawback particularly for carbene complexes containing bulky alkoxy groups. This is consistent with the fact that all the methylenation attempts on chiral alkenyl carbene complexes with diazomethane and chloromethylithium resulted exclusively in the dipolar [3+2]- and [2+1]-cycloaddition reactions, respectively (Scheme 2, eq. 2).^{8,9}



Scheme 2. The reaction of Fischer carbene complexes with methylenating reagents.

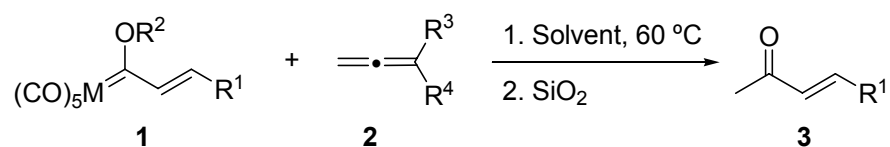
Herein we report that commercially available dimethylallene thermally reacts with achiral and chiral alkoxy-carbene complexes of chromium to produce high yields of 2-alkoxy-1,3-dienes. This is the first metathesis reaction of transition-metal carbenes with allenes hitherto reported.¹⁰ This result complements our own results on the rhodium-catalyzed and nickel-mediated reactions of allenes and Fischer carbene complexes which provide five- and seven-membered carbocycles.¹¹

Results and Discussion

We started by treating the chromium carbene complex **1a** ($M = \text{Cr}$, $R^1 = p\text{-CH}_3\text{OC}_6\text{H}_4$; $R^2 = \text{Me}$) with dimethylallene **2a** ($R^3 = R^4 = \text{Me}$, 3 equiv) in THF at 60° C (Table 1, entry 1). Gratifyingly, 4-(4-methoxyphenyl)-3-buten-2-one **3a** was formed in 63% yield after stirring for 2 h and silica gel chromatographic purification. Therefore, the methylenation reaction is followed, under the purification conditions, by the enol ether hydrolysis to furnish the corresponding enone. Then

some reaction variables, e. g. solvent, allene, and metal carbene, were checked. It was found that, although a number of solvents gave satisfactory results (entries 1-4), the best yield for compound **3a** was achieved with 1,2-dichloroethane (DCE) (entry 4). Similar yields were reached for phenyl, 4-chlorophenyl and ferrocenyl substituted carbene complexes (entries 5-7). Remarkably, the methylenation/hydrolysis sequence of a metal carbene having a bulky alkoxy group occurred with the highest yield (entry 8). The use of 1,1-diphenylallene (entries 9 and 10) and phenylallene (entry 11) was unsuccessful as lower yield and a complex mixture, respectively, were obtained. Lastly, the chromium carbene complexes led to significant higher yields than their tungsten analogs (entry 5 vs entry 12).

Table 1. Thermal reaction of alkenyl carbene complexes **1** and allenes **2**



Entry	M	R ¹	R ²	R ³	R ⁴	Solvent	3 (yield) ^a
1	Cr	<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	CH ₃	CH ₃	THF	3a (63)
2	Cr	<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	CH ₃	CH ₃	Toluene	3a (62)
3	Cr	<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	CH ₃	CH ₃	Hexane	3a (61)
4	Cr	<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	CH ₃	CH ₃	DCE ^b	3a (82)
5	Cr	C ₆ H ₅	CH ₃	CH ₃	CH ₃	DCE	3b (80)
6	Cr	<i>p</i> -ClC ₆ H ₄	CH ₃	CH ₃	CH ₃	DCE	3c (91)
7	Cr	Ferrocenyl	CH ₃	CH ₃	CH ₃	DCE	3d (84)
8	Cr	C ₆ H ₅	Ment ^c	CH ₃	CH ₃	DCE	3b (95)
9	Cr	<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	C ₆ H ₅	C ₆ H ₅	DCE	3a (58)
10	Cr	C ₆ H ₅	CH ₃	C ₆ H ₅	C ₆ H ₅	DCE	3b (65)
11	Cr	C ₆ H ₅	CH ₃	C ₆ H ₅	H	DCE	- ^d
12	W	C ₆ H ₅	CH ₃	CH ₃	CH ₃	DCE	3b (54)

^a Isolated yields based on alkenyl carbene complexes **1**.

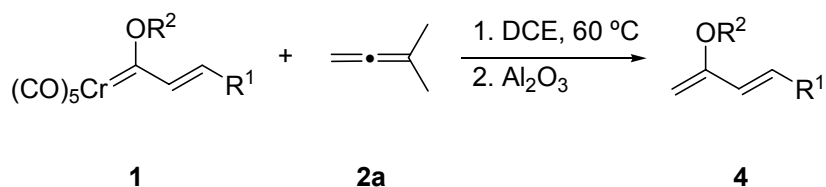
^b DCE = 1,2-dichloroethane.

^c Ment = (1*R*, 2*S*, 5*R*/1*S*, 2*R*, 5*S*)-Menthyl.

^d A complex mixture of compounds was obtained.

At this point it was desired to set up the conditions to stop the reaction at the alkoxydiene stage. This was brought about by simply running the reaction under the above conditions (3 equiv of allene, DCE, 60°C, 2-5 h) followed by solvent removal and chromatographic purification using Al₂O₃ and a 10:1 mixture of hexane-ethyl acetate as the eluent. The achiral and chiral dienes thus prepared are depicted in Table 2. First, 2-methoxy-1,3-butadienes **4a-c** were synthesized in 79-84% yield from the corresponding methoxycarbene complexes **1** and 1,1-dimethylallene **2a** (entries 1-3). Interestingly, this methodology allowed for the efficient preparation of racemic and nonracemic chiral dienes **4d-f** from carbene complexes derived from chiral alcohols, like (±)-menthol (entries 4 and 5) and (-)-8-phenylmenthol (entry 6). In all the cases the *E*-diene derivatives (*J*_{H(3)-H(4)} = 15-16 Hz) were obtained with excellent yields (90-94%) and without *E/Z* isomerization.

Table 2. Synthesis of 2-alkoxy-1,3-butadienes **4** from chromium alkenylcarbene complexes **1** and dimethylallene **2a**



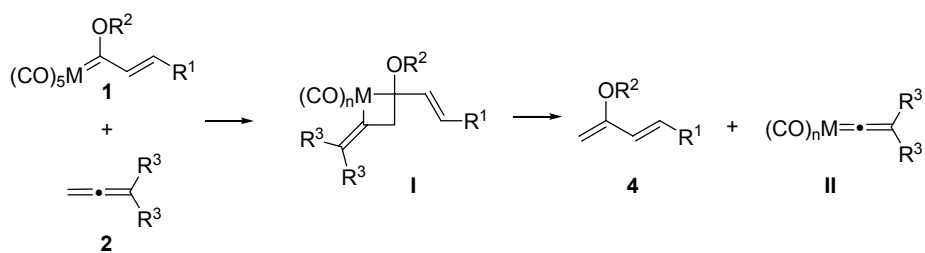
Entry	R ¹	R ²	4 (yield) ^a
1	<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	4a (79)
2	C ₆ H ₅	CH ₃	4b (84)
3	<i>p</i> -ClC ₆ H ₄	CH ₃	4c (81)
4	C ₆ H ₅	Ment ^b	4d (90)
5	2-Furyl	Ment ^b	4e (92)
6	C ₆ H ₅	PhMent ^b	4f (94)

^a Isolated yields from alkenyl carbene complexes **1**.

^b Ment = (1*R*, 2*S*, 5*R*/1*S*, 2*R*, 5*S*)-Menthyl, PhMent = (1*R*, 2*S*, 5*R*)-8-Phenylmenthyl.

The formation of compounds **4** can be explained by the chemo- and regioselective [2+2]-cycloaddition between the M=C function and the less substituted allene C=C double-bond to form the metallacyclobutane intermediate **I** (Scheme 3). The latter would evolve through a retro [2+2]-cycloaddition to provide the 2-alkoxy-1,3-butadiene structure **4**. The accompanying metal vinylidene species **II** could be neither isolated nor trapped with alcohols. It is noteworthy that this metathesis reaction is a rather unusual process for alkoxy carbenes.¹² Moreover, it represents

a new reaction pathway for Fischer carbene complexes towards allenes which differs from those previously reported.¹⁰



Scheme 3. Mechanism for the formation of alkoxydienes **4** from alkenyl carbene complexes **1** and allenes **2**.

In conclusion, we have developed a new methylenation reaction of alkenyl Fischer carbene complexes based on a rather unusual metathesis reaction with allenes. From a synthetic point of view, this approach provides an appropriate entry into useful achiral and chiral building blocks, such as (*E*)-4-substituted-2-alkoxy-1,3-carbodienes. The availability and handling of the starting materials and the ease of the experimental make this one-step procedure preferable over those previously reported.

Experimental Section

General Procedures. 1H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$, on a Bruker AC-300 (300 and 75.5 MHz) and Bruker AMX-400 (400 and 100 MHz) spectrometers. Chemical shifts are given in ppm relative to TMS (1H , 0.0 ppm) or $CDCl_3$ (^{13}C , 77.0 ppm). Carbon multiplicities were assigned by DEPT techniques. Elemental analyses were carried out on a Perkin-Elmer 2400 and Carlo Erba 1108 microanalyzers.

TLC was performed on aluminum-backed plates with silica gel 60 with F_{254} indicator. All reactions were carried out under nitrogen using standard Schlenck techniques. 1,2-dichloroethane was distilled from CaH_2 . Fischer carbene complexes **1** and 1,1-diphenylallene were prepared according to literature methods. All other reagents and solvents used in this work were of the best commercial grade available and used without further purification.

General procedure for the thermal reaction of alkenyl Fischer carbene complexes **1** and allenes **2**. Synthesis of enone derivatives **3** and alkoxydienes **4**

A solution of the carbene complex **1** (0.5 mmol) and 1,1-dimethylallene (1.5 mmol) in DCE (5 mL) was stirred in a sealed tube at 60° C until disappearance of the starting carbene complex (checked by TLC; 2-5 h). The solvent was then removed under reduced pressure and final

chromatographic purification of the resulting residue afforded compounds **3** (SiO₂; 10:1 mixture of hexane:ethyl acetate) or dienes **4** (Al₂O₃; 10:1 mixture of hexane:ethyl acetate).

(E)-4-(4-Methoxyphenyl)-3-buten-2-one (3a). Yellowish oil, ¹H-NMR (CDCl₃): 2.38 (s, 3H), 3.87 (s, 3H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 7.47-7.53 (m, 3H); ¹³C-NMR (CDCl₃): 27.3 (CH₃), 55.3 (CH₃), 114.3 (CH), 124.9 (CH), 126.9 (C), 129.8 (CH), 143.1 (CH), 161.5 (C), 198.3 (C). Anal. Calcd for C₁₁H₁₂O₂: C, 74.98; H, 6.86; Found: C, 75.04; H, 6.88.

(E)-4-Phenyl-3-buten-2-one (3b). Colorless oil, ¹H-NMR (CDCl₃): 2.41 (s, 3H), 6.74 (d, *J* = 16.2 Hz, 1H), 7.41-7.43 (m, 3H), 7.51-7.56 (m, 3H); ¹³C-NMR (CDCl₃): 27.5 (CH₃), 127.0 (CH), 128.2 (CH), 128.9 (CH), 130.5 (CH), 134.3 (C), 143.4 (CH), 198.4 (C). Anal. Calcd for C₁₀H₁₀O: C, 82.16; H, 6.89; Found: C, 82.07; H, 6.85.

(E)-4-(4-Chlorophenyl)-3-buten-2-one (3c). Yellowish oil, ¹H-NMR (CDCl₃): 2.41 (s, 3H), 6.71 (d, *J* = 16.5 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.44-7.52 (m, 3H); ¹³C-NMR (CDCl₃): 27.7 (CH₃), 127.5 (CH), 129.3 (CH), 129.4 (CH), 132.9 (C), 136.4 (C), 141.8 (CH), 198.1 (C). Anal. Calcd for C₁₀H₉ClO: C, 66.49; H, 5.02; Found: C, 66.61; H, 4.98.

(E)-4-Ferrocenyl-3-buten-2-one (3d). Orange oil, ¹H-NMR (CDCl₃): 2.29 (s, 3H), 4.15 (s, 5H), 4.44 (m, 2H), 4.50 (m, 2H), 6.33 (d, *J* = 15.9 Hz, 1H), 7.42 (d, *J* = 15.9 Hz, 1H); ¹³C-NMR (CDCl₃): 27.1 (CH₃), 68.7 (CH), 69.7 (CH), 71.2 (CH), 78.5 (C), 124.6 (CH), 145.1 (CH), 197.8 (C). Anal. Calcd for C₁₄H₁₄FeO: C, 66.17; H, 5.55; Found: C, 66.32; H, 5.61.

(E)-3-Methoxy-1-(4-methoxyphenyl)buta-1,3-diene (4a). Yellowish oil, ¹H-NMR (CDCl₃): 3.70 (s, 3H), 3.81 (s, 3H), 4.22 (s, 2H), 6.45 (d, *J* = 16.1 Hz, 1H), 6.84-6.91 (m, 3H), 7.37 (d, *J* = 8.7 Hz, 2H); ¹³C-NMR (CDCl₃): 54.9 (CH₃), 55.3 (CH₃), 86.2 (CH₂), 114.1 (CH), 122.6 (CH), 127.9 (CH), 128.2 (CH), 129.6 (C), 159.4 (C), 159.5 (C). Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42; Found: C, 75.69; H, 7.53.

(E)-3-Methoxy-1-phenylbuta-1,3-diene (4b). Colorless oil, ¹H-NMR (CDCl₃): 3.73 (s, 3H), 4.29 (s, 2H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 7.25-7.47 (m, 5H); ¹³C-NMR (CDCl₃): 54.5 (CH₃), 86.9 (CH₂), 124.5 (CH), 126.5 (CH), 127.5 (CH), 128.4 (CH), 128.6 (CH), 136.6 (C), 159.1 (C). Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55; Found: C, 82.41; H, 7.56.

(E)-1-(4-Chlorophenyl)-3-methoxybuta-1,3-diene (4c). Yellowish oil, ¹H-NMR (CDCl₃): 3.70 (s, 3H), 4.28 (s, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.88 (d, *J* = 15.8 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H); ¹³C-NMR (CDCl₃): 54.9 (CH₃), 87.7 (CH₂), 125.2 (CH), 127.4 (CH), 127.8 (CH), 128.7 (CH), 133.3 (C), 135.3 (C), 158.9 (C). Anal. Calcd for C₁₁H₁₁ClO: C, 67.87; H, 5.70; Found: C, 67.93; H, 5.58.

(E) (1R, 2S, 5R/1S, 2R, 5S)-3-Menthyloxy-1-phenylbuta-1,3-diene (4d). Yellowish oil, ¹H-NMR (CDCl₃): 0.92 (d, *J* = 6.9 Hz, 3H), 1.05-1.27 (m, 8H), 1.53-1.84 (m, 5H), 2.33 (m, 2H), 4.01 (m, 1H), 4.33 (s, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 7.23-7.56 (m, 5H); ¹³C-NMR (CDCl₃): 16.8 (CH₃), 20.7 (CH₃), 22.2 (CH₃), 23.8 (CH₂), 26.3 (CH), 31.4 (CH), 34.6 (CH₂), 39.6 (CH₂), 47.9 (CH), 76.4 (CH), 87.6 (CH₂), 125.9 (CH), 126.6 (CH), 127.5 (CH), 128.3 (CH), 128.5 (CH), 136.9 (C), 157.0 (C). Anal. Calcd for C₂₀H₂₈O: C, 84.45; H, 9.92; Found: C, 84.56; H, 9.85.

(E) (1R, 2S, 5R/1S, 2R, 5S)-1-(2-Furyl)-3-Menthyloxybuta-1,3-diene (4e). Yellowish oil, $^1\text{H-NMR}$ (CDCl_3): 0.92-1.76 (m, 16H), 2.45 (m, 2H), 4.06 (m, 1H), 4.39 (s, 1H), 4.40 (s, 1H), 6.23 (m, 2H), 6.91 (d, $J = 15.7$ Hz, 1H), 7.25 (d, $J = 15.7$ Hz, 1H), 7.38 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3): 17.0 (CH_3), 20.8 (CH_3), 22.3 (CH_3), 24.1 (CH_2), 26.7 (CH), 31.4 (CH), 34.8 (CH_2), 39.8 (CH_2), 48.3 (CH), 76.4 (CH), 88.1 (CH_2), 109.3 (CH), 111.8 (CH), 116.9 (CH), 125.0 (CH), 142.4 (CH), 153.4 (C), 157.1 (C). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2$: C, 78.79; H, 9.55; Found: C, 78.91; H, 9.53.

(E) (1R, 2S, 5R)-1-Phenyl-3-(8-phenylmenthyloxy)buta-1,3-diene (4f). Yellowish oil, $^1\text{H-NMR}$ (CDCl_3): 0.7 (d, 3H), 0.93-1.21 (m, 6H), 1.36 (s, 3H), 1.50 (s, 3H), 2.07 (m, 1H), 2.33 (m, 1H), 4.10 (m, 1H), 4.21 (s, 1H), 4.33 (s, 1H), 6.52 (d, $J = 15.9$ Hz, 1H), 6.74 (d, $J = 15.9$ Hz, 1H), 7.06-7.45 (m, 10H); $^{13}\text{C-NMR}$ (CDCl_3): 22.7 (CH_3), 27.4 (CH_3), 28.0 (CH_3), 28.6 (CH_3), 32.0 (CH), 35.8 (CH_2), 40.4 (CH_2), 40.9 (C), 52.4 (CH), 77.4 (CH), 88.0 (CH_2), 126.2 (CH), 126.8 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 128.9 (CH), 129.5 (CH), 129.8 (CH), 138.1 (C), 152.1 (C), 157.0 (C). Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{O}$: C, 86.62; H, 8.95; Found: C, 86.73; H, 8.91.

Acknowledgements

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