

Preliminary Communication

Oxidative cleavage of metal carbene complexes by iodine

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Abstract

Oxidative cleavage of cyclic diamino-substituted group VI metal carbene complexes with iodine under thermal conditions provides imidazolidin-2-ylidinium iodides and the related six-membered derivatives in moderate to good yields. © 1997 Elsevier Science S.A.

Keywords: Metal carbene complexes; Iodine; Oxidative cleavage; Group VI metals; Imidazolidin-2-ylidinium iodides

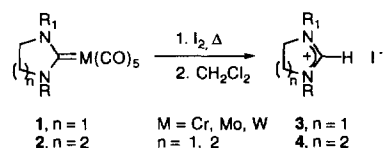
1. Introduction

Conversion of metal carbenes into useful organic functionalities is an important area of research in synthetic application [1]. In this track the reaction of metal carbene complexes with halogens to provide the corresponding organic halides is rarely reported [2–4]. In pursuing the synthetic application of metal carbene complexes, we previously reported the synthesis of group VI metal carbene complexes by deoxygenation reaction of $M(CO)_6$ with $RNH(CH_2)_nN = PPh_3$ to form the isocyanide complex, which subsequently underwent intramolecular cyclization to give $(CO)_5M = \overline{C}N(R)(CH_2)_nNH$ [5]. In this report we describe the cleavage of $M = C$ bonds of cyclic diamino-substituted group VI metal carbenes with iodine to provide the organic iodides in reasonable isolated yields.

2. Results and discussion

Carbene complexes used in this study were prepared according to the method reported previously [5]. A mixture of metal carbene complexes and iodine (1.5 equiv.) were heated in a flask at 120°C under vacuum for 20 min. Upon cooling, the reaction mixture was extracted with dichloromethane (Eq. (1)). ¹H NMR spectrum of the extracted material shows only one

single organic product formed. The extract was chromatographed on silica gel with elution of dichloromethane and ethyl acetate. Evaporation of the elute yields the light-yellow color liquid as the desired compound which is essentially identical to the species first extracted from the reaction. Results are presented in Table 1 [6] and all yields reported are isolated ones. The products were formed from chromium-, molybdenum-, and tungsten-carbene complexes, and the yields were not affected by the metal employed.



1, n = 1 M = Cr, Mo, W 3, n = 1
2, n = 2 n = 1, 2 4, n = 2

(1)

The ionic form of the product is based on the conductivity measurement and ¹³C NMR spectroscopic analysis. Conductivity of **3a** in acetone is 96 ohm⁻¹cm²mol⁻¹ which verifies the 1:1 electrolyte of the product in solution. In addition, the ¹³C NMR chemical shift of unique carbon in **3a** appears at 156.7 ppm, indicating a sp² hybridization for iminium carbon center. These observations along with analytic data confirm the structure proposed for the product. Concerning the hydrogen source, it is noted that 85% deuterium-labeled **3a-d₁** (45% isolated yield) was obtained when the reaction was run thermally in the absence of solvent followed by the extraction with CH₃OD. The deuterium-labeled product is also obtained

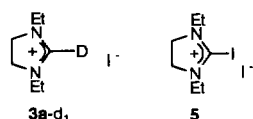
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Table 1
Results of oxidative cleavage of metal carbene complexes by iodine

Complex	Product	isolated yield
1a R = R ₁ = Et M = Cr	3a R = R ₁ = Et	41 %
1b R = R ₁ = Et M = Mo	3a	52 %
1c R = R ₁ = Et M = W	3a	57 %
1d R = R ₁ = allyl M = Mo	3b R = R ₁ = Allyl	56 %
1e R = R ₁ = allyl M = W	3b	58 %
2a R = R ₁ = Me M = W	4a R = Me R ₁ = Me	64 %
2b R = Me R ₁ = allyl M = W	4b R = Me R ₁ = allyl	56 %
2c R = H R ₁ = Me M = Cr	4c R = H R ₁ = Me	63 %
2d R = H R ₁ = Me M = Mo	4c	65 %
2e R = H R ₁ = Et M = Cr	4d R = H R ₁ = Et	69 %
2f R = H R ₁ = Et M = Mo	4d	64 %
2g R = H R ₁ = Et M = W	4d	53 %
2h R = H R ₁ = allyl M = W	4e R = H R ₁ = allyl	61 %

Reaction conditions: A mixture of complex and iodine (in a molar ratio of 1:3) was heated at 120°C under vacuum for 20 min. Upon cooling, dichloromethane was then added to extract the product.

by using CD₂Cl₂. These results illustrate that the hydrogen comes from the solvent used for extraction.



When reactions of **1a** with I₂ (3 equivmol) were

carried out in chloroform solutions at 25°C, both chromium and molybdenum carbene complexes (**1a** and **1b**) provided 2-iodo-1,3-diethylimidazolidin-2-ylidinium iodide **5** [7] as the product without formation of **3a** [2]. But the tungsten complex **1c** still granted **3a** as the product in a poor yield. This study demonstrates a useful method for conversion of metal carbene species into organic iodides. The detailed mechanistic problem of this oxidative cleavage and potential applications of these iodides for organic synthesis are under investigation.

Acknowledgements

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- [6] All new compounds were characterized on the basis of ¹H NMR, ¹³C NMR, and elemental analyses, and satisfactory results were obtained. Selected spectral data for **3a** as typical: δ_H (CDCl₃) 9.09 (s, 1H, -NCHN-), 3.98 (s, 4 H, -CH₂N-), 3.60 (q, J = 7.2 Hz, 4 H, -CH₂CH₃), 1.31 (t, J = 7.2 Hz, 6 H, -CH₃); δ_C (CDCl₃) 156.7, 48.4, 43.4, 13.0; Anal. Calcd for C₇H₁₅N₂I: C, 33.09; H, 5.95; N, 11.02. Found C, 33.12; H, 5.62; N, 11.15.
- [7] Compound **5**: a yellow solid; δ_H (CDCl₃) 4.04 (s, 4 H, -CH₂N), 3.67 (q, J = 7.2 Hz, 4 H, -CH₂CH₃), 1.26 (t, J = 7.2 Hz, 6 H, -CH₃); δ_C (CDCl₃) 142.4 (-NCN-), 48.7 (-CH₂CH₃), 46.5 (-CH₂N), 13.0 (-CH₃); Anal. Calcd for C₇H₁₄N₂I₂: C, 22.13; H, 3.71; N, 7.37. Found C, 22.16; H, 3.52; N, 7.25.