Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters 46 (2005) 2453–2455
ELSEVIER
Tetrahedron Letters

A silver-catalyzed Büchner reaction

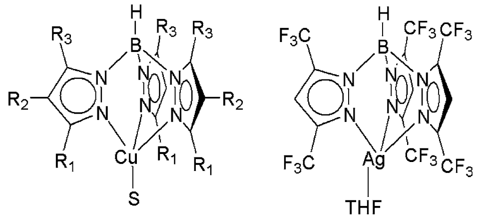
Carl J. Lovely,* R. Greg Browning, Vivek Badarinarayana and H. V. Rasika Dias*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, USA

Received 16 November 2004; revised 8 February 2005; accepted 9 February 2005

Abstract—A silver scorpionate complex, derived from the highly fluorinated $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, catalyzes the addition of ethyl diazoacetate to benzene rings, providing norcaradienes, which undergo electrocyclization to provide the corresponding cycloheptatriene. These reactions are surprisingly selective for addition to the aromatic moiety rather than C–H insertion.

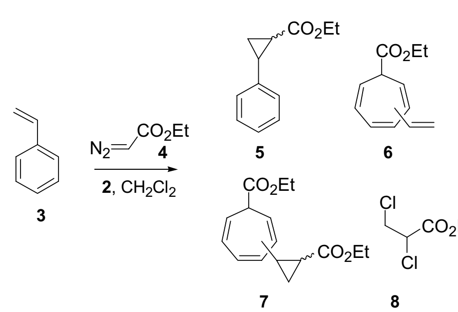
Some time ago, we initiated a program to investigate the catalytic potential of several metal complexes derived from highly fluorinated analogs (e.g., **1a** and **2**) of the classical tris(pyrazolyl)borate (scorpionate) ligands.[1] Along these lines, our labs have established that the copper(I) complexes (e.g., **1a**) are effective nitrene transfer agents[2] and carbene transfer agents,[3] providing aziridines and cyclopropanes, respectively, from alkenes, and C–H insertion products with alkanes. More recently we have examined the ability of the related silver(I) adduct **2** to function as a nitrene and carbene transfer catalyst (Fig. 1). Although we have not demonstrated that nitrene transfer reactions are feasible with this complex,[4] it effectively catalyzes carbene insertion reactions into C–H and C–X (X = Cl, Br) bonds.[3,5,6]



1a: $R_1 = R_3 = CF_3$, $R_2 = H$
1b: $R_1 = R_2 = R_3 = Br$
1c: $R_1 = Mes$, $R_2 = R_3 = H$
2

Figure 1. Scorpionate catalysts.

In a continuation of these efforts we attempted to extend the chemistry of this latter complex, by examining its utility in cyclopropane formation by carbenoid addition to alkenes. On treatment of a dichloromethane solution of styrene with ethyl diazoacetate (**4**, EDA) in the presence of 5 mol % of **2**, a reaction took place as evidenced by the liberation of nitrogen. However, analysis of the surprisingly complex ^1H NMR spectrum of the crude reaction mixture indicated that the anticipated simple addition to the olefinic bond was not the major product (Scheme 1, **3** + **4** → *cis*/*trans* **5**). There were several unexpected signals, other than unreacted styrene, in the vinylic region of the spectrum that initially could not be accounted for. However on further analysis it became clear that, in addition to the expected cyclopropane, addition to the aromatic moiety had occurred followed by a ring expansion, that is, a Büchner reaction had taken place (Scheme 1).[7,8] It should be noted that in addition to the ring expansion product, insertion of the carbene into the C–Cl bond of dichloromethane had occurred.[5] To simplify matters, the reaction was conducted



Scheme 1.

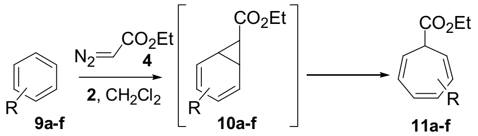
Keywords: Carbene; Scorpionates; Catalysis; Ring-expansion.

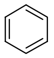
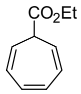
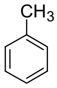
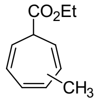
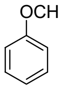
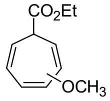
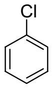
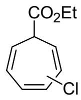
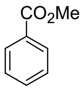
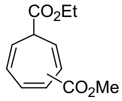
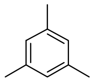
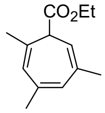
* Corresponding authors. Tel.: +1 817 272 5446; fax: +1 817 272 3808 (C.J.L.); tel.: +1 817 272 3813; fax: +1 817 272 3808 (H.V.R.D.); e-mail addresses: lovely@uta.edu; dias@uta.edu

doi:10.1016/j.tetlet.2005.02.052

using benzene as a substrate, and much to our delight, a single cycloheptatriene product (**11a**) was obtained in 74% yield (Table 1). A small quantity of the C–Cl insertion product **8** was also obtained (ca. 25%), so to prevent this competing reaction pathway, the reaction was repeated in neat benzene, under these conditions the ring expansion product was obtained in a comparable 75% yield (based on EDA).

Table 1. Yields and isomer ratios of the silver catalyzed Büchner[9] reaction benzene derivatives and EDA



Substrate	Product	Yield[a,b] (%)	Isomer ratio (2:3:4)
 **9a**	 **11a**[10,11]	74 75[c]	N/A N/A
 **9b**	 **11b**[11]	64[d] 62[c,e]	1:1.8:2.4
 **9c**	 **11c**[12]	40	1:0:19
 **9d**	 **11d**[12]	49[f]	1:8.5:18
 **9e**	 **11e**[12]	14[f]	0:1:1
 **9f**	 **11f**[11]	35[g]	N/A

[a] The yields are the average of at least two runs and refer to isolated material and, unless noted, were conducted in CH_2Cl_2.

[b] In the reactions conducted in CH_2Cl_2, there was 15-25% of the C–Cl insertion product **8** observed in the ^1H NMR spectrum of the crude reaction mixture.

[c] These reactions were conducted in the neat arene.

[d] 4% of the C–H insertion product was observed in the ^1H NMR spectrum of the crude reaction mixture.

[e] 5% of the C–H insertion product was observed in the ^1H NMR spectrum of the crude reaction mixture.

[f] The purified material was contaminated with ca. 5% of the C–Cl insertion product.

[g] 28% of the C–H insertion product **13** was observed in the ^1H NMR spectrum of the crude reaction mixture.

Given that these reaction conditions initiated the addition and rearrangement with benzene, the generality of the reaction with substituted derivatives was investigated. As can be seen in Table 1, both electron rich and electron deficient systems participate in the rearrangement, but with varying efficiencies and selectivities (vis à vis isomer distribution).

In general, the more electron rich systems react with better efficiencies than the more electron poor systems, although all substituents appear to lead to reduced yields compared to the parent substrate. This latter observation is in keeping with the electrophilic nature of these metallocarbenoid systems. These observations parallel the results obtained by Noels and co-workers with rhodium catalysts, but the yields are lower.[10,13] Pérez and co-workers have reported that related complexes **1b** and **1c** will catalyze carbene transfer to aromatics.[11] In their studies with alkylbenzenes it was found that both addition (formation of **11**) and benzylic C–H insertion were observed to varying extents, depending on the catalyst. With catalyst **2**, no evidence of aryl C–H insertion was noted and only in the reaction of **9b** was a small amount of benzylic C–H insertion (Fig. 2, **12**), ca. 4–5%, observed in the ^1H NMR spectrum of the crude reaction mixture. In a related study it has been demonstrated that this complex is an effective catalyst for C–H insertion and so the selectivity for the Büchner pathway is quite interesting.[3] To probe this issue further, the reaction of mesitylene under these conditions was investigated. Interestingly, the major pathway was again the Büchner reaction, although C–H insertion did occur to an appreciable extent ca. 28%. The selectivity for the Büchner pathway is quite remarkable when this outcome is normalized for the number of reactive sites, which suggest that addition to C=C occurs ca. 2–7×'s faster than C–H insertion. In addition to chemoselectivity issues, these addition–rearrangement reactions can give rise to up to three regioisomeric products. In general our results mirror those of Noels and co-workers and Pérez and co-workers,[10,11] with the 4-isomer predominating, although the scorpionate systems appear to give rise to a greater proportion of the 3-isomer compared to the rhodium systems.

In conclusion, we have discovered a novel silver-catalyzed carbene addition reaction that proceeds in good to moderate yields. Silver-catalyzed homogeneous processes of any type are rare,[6] and to our knowledge, this study represents the first use of silver(I) in Büchner

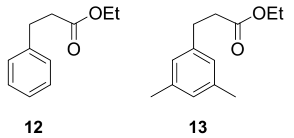


Figure 2. C–H insertion products from **9b** and **9f**.

chemistry. Typically, rhodium(II) compounds are the most widely used catalysts for this important process.[8] The yields of silver scorpionate mediated process appear to be somewhat lower than with the rhodium-based systems, but this may be due to the slow decomposition of **2**. The presence of a B–H moiety presumably leads to reduction of the Ag(I) to Ag(0), and attendent loss of activity.[1] Current efforts are focused on identifying catalysts that retain the reactivity of **2**, but are more stable.

Acknowledgements

This work was supported by the Robert A. Welch Foundation (Y-1362 (C.J.L.) and Y-1289 (H.V.R.D.)) and NSF (CHE-0314666 for H.V.R.D.). The NSF (CHE-9601771) is thanked for partial funding of the purchase of a 500 MHz NMR spectrometer.

References and notes

1. Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College: London, 1999; Pettinari, C.; Santini, C. In *Comprehensive Coordination Chemistry II*; Elsevier, 2004; Vol. 1, pp 159–210.
2. Dias, H. V. R.; Lu, H.-L.; Polach, S. A.; Goh, T.; Browning, R. G.; Lovely, C. J. *Organometallics* **2002**, *21*, 1466.
3. Dias, H. V. R.; Browning, R. G.; Richey, S. A.; Lovely, C. J. *Organometallics* **2004**, *23*, 1200.
4. (a) Cui, Y.; He, C. *J. Am. Chem. Soc.* **2003**, *125*, 16202; (b) Cui, Y.; He, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 4210.
5. Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V.; Lovely, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 9270–9271.
6. For other silver catalyzed processes see citations in Ref. 3. Also see: (a) Sweis, R. F.; Schramm, M. P.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7442; (b) Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 9993; (c) Bachmann, S.; Fielenbach, D.; Anker Jørgensen, K. *Org. Biomol. Chem.* **2004**, 4210.
7. The Büchner reaction is the thermal or photochemically induced carbene addition to an aromatic, forming a norcaradiene derivativem followed by ring expansion to provide a cycloheptatriene. Typically, under these conditions mixtures of conjugated and non-conjugated isomers are obtained. Büchner, E.; Curtius, T. *Chem. Ber.* **1885**, *18*, 2371.
8. Transition metal catalyzed variants of the Büchner reaction are known, and tend to produce non-conjugated isomers due to the generally milder conditions employed. For some recent papers see: (a) Pirrung, M. C.; Liu, H.; Morehead, A. T., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 1014; (b) Merlic, C. A.; Zechman, A. L.; Miller, M. M. *J. Am. Chem. Soc.* **2001**, *123*, 11101; (c) Yang, M.; Webb, T. R.; Livant, P. *J. Org. Chem.* **2001**, *66*, 4945; (d) Doyle, M. P.; Ene, D. G.; Forbes, D. C.; Pillow, T. H. *Chem. Commun.* **1999**, 1691; (e) Maguire, A. R.; Buckley, N. R.; O'Leary, P.; Ferguson, G. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4077; (f) Moody, C. J.; Miah, S.; Slawin, A. M. Z.; Mansfield, D. J.; Richards, I. C. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4067; (g) Manitto, P.; Monti, D.; Zanzola, S.; Speranza, G. *J. Org. Chem.* **1997**, *62*, 6658.
9. General procedure: Ethyl diazoacetate (114 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) was added by syringe pump over 4 h to a stirred solution of the arene **9** (5.00 mmol) and **2** (40 mg, 0.05 mmol) in CH_2Cl_2 (1.5 mL) under nitrogen in a flask shielded from light. The resulting solution was stirred overnight at room temperature under nitrogen, diluted with CH_2Cl_2 (20 mL), filtered through Celite, and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, 4:1 hexanes/ether) to give the cycloheptatriene **11** (and C–Cl insertion product **8**) as a colorless oil.
10. Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssié, P. *J. Org. Chem.* **1981**, *46*, 873.
11. Morilla, M. E.; Diaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Perez, P. J. *Organometallics* **2004**, *23*, 293.
12. The spectroscopic data for these compounds is essentially identical to that obtained for the corresponding Büchner products derived from methyl diazoacetate, Ref. 10. Selected ^1H NMR (500 MHz, $CDCl_3$) data for: **11c** (4-isomer) δ = 6.20 (ddd, J = 8.1, 6.7, 1.2 Hz, 1H), 6.07 (ddd, J = 9.9, 1.7, 1.7 Hz, 1H), 5.86 (dd, J = 6.7, 2.0 Hz, 1H), 5.61 (dd, J = 9.9, 5.9 Hz, 1H), 5.26 (ddd, J = 10.0, 5.2, 0.7 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.66 (s, 3H), 2.69 (dd, J = 5.5, 5.5 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). Compound **11d** (4-isomer) δ = 6.81 (dd, J = 6.4, 1.0 Hz, 1H), 6.59 (ddd, J = 11.4, 5.7, 0.5 Hz, 1H), 5.53–5.46 (m, 2H), 5.20–5.14 (m, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.71 (ddd, J = 6.0, 5.9, 1.3 Hz, 1H), 1.30 (t, J = 7.2 Hz, 2H); (3-isomer) = 6.58 (ddd, J = 10.9, 5.7, 0.5 Hz, 1H), 6.47–6.45 (m, 1H), 6.42-6.38 (m, 1H), 6.32 (dd, J = 9.4, 5.7 Hz, 1H), 5.76 (dd, J = 8.2, 7.6 Hz, 1H), 4.24 (q, J = 7.4 Hz, 2H), 2.48 (ddd, J = 5.7, 5.0, 0.7 Hz, 1H), 1.27 (t, J = 7.4 Hz, 3H). **11e** (1:1 mixture of 3- and 4-isomers) = 7.20–7.16 (m, 1H), 7.00–6.90 (m, 1H), 6.86–6.80 (m, 1H), 6.63 (dd, J = 10.1, 6.5 Hz, 1H), 6.42–6.36 (m, 2H), 5.71–5.69 (m, 1H), 5.52 (ddd, J = 8.9, 5.5, 1.5 Hz, 1H), 5.34–5.31 (m, 1H), 4.82–4.78 (m, 1H), 4.27 (q, J = 7.1 Hz, 4H), 3.83 (s, 3H), 3.79 (s, 3H), 1.32–1.26 (m, 6H). For the corresponding conjugated isomers of **11c** see: Garst, M. E.; Roberts, V. A. *J. Org. Chem.* **1982**, *47*, 2188.
13. This can be explained in part due to differences in the reaction conditions employed. In Noels' work, the aryl system was used as both substrate and solvent, whereas in this work the reactions were conducted in CH_2Cl_2 in most cases.