Substrate Dependence of Benzene vs Furan Ring Formation in the Reaction of Iron(0) Carbene Complexes with Alkynes[1]

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Transition-metal carbene complexes[2] have been the subject of intense scrutiny. Of special interest is their benzannulation reaction with alkynes,[3] which has inspired many variations.[4] This process is a powerful tool for the synthesis of highly substituted aromatic rings.[5] Wulff studied the sensitivity of this reaction to the presence of donor or acceptor substituents on the aromatic ring of the complex.[6] Herein we report the first examples of this transformation with iron(0) carbene complexes.[7] Furan annulation[8] is the major alternate reaction. Semmelhack discovered that alkynes form η^4-pyrone iron complexes[9] with alkoxy(carbene)iron(0) complexes and furans[10] with amino(carbene)iron(0) complexes.

The iron(0) carbene complexes **1**–**4** were prepared[11] in yields of 27–65%. The order of stability to oxidation was (2-ethylphenyl)methylene (**2b**) > **4** > **1** > **3** > **2a**. Complexes **1**, **3**, and **4** had spectroscopic properties typical of iron carbene complexes; **2a** exhibited an unexpected temperature dependence of its NMR spectra. At −80 °C, the broad methylene absorptions were observed at 4.25 and 5.27 ppm; upon warming of the complex sample to +25 °C, a broad peak at 4.68 ppm was observed, with coalescence occurring at −20 °C. This phenomenon was reversible and was probably due to the (*E*) and (*Z*) rotamers about the C(carbene)–O bond.[12] The ^{13}C NMR spectrum exhibited a similar temperature dependence. Although chelation of metals by *o*-methoxy groups is well known,[13] we could not convert **2a** to the chelated form.[14] We originally believed that the extreme sensitivity of the carbene complex and the dynamic NMR behavior were consequences of unfavorable steric interactions between the carbene and alkoxy moiety, but the remarkably robust complex **2b** survived heating at +45 °C with little (<10%) decomposition over 1 h. Its spectrum was well resolved (ca. 0.5 Hz), with slight line broadening of the methylene CH_2 resonance which became sharper at +45 °C. Resonance stabilization of **2a** is sterically inhibited, while inductive stabilization by the ethyl group of **2b** is not adversely affected.

The reaction of electron-poor alkynes with chromium carbene complexes usually gives low yields of benzannulation products.[15] Yamashita has shown that such alkynes can form benzene rings.[16] We found THF to be the preferred solvent for effecting benzannulation of **1** with dimethylacetylene dicarboxylate (DMAD). To probe electronic effects, the methoxy group was chosen because it can be a resonance donor in the *para* position, an inductive acceptor in the meta position, or a chelating ligand (and resonance donor) in the ortho position. Our benzannulation results are shown in Table I. Neither pyrone complexes nor indenes were detected, and the alkyne cyclotrimer was a minor contaminant. A 5–10-fold excess of DMAD gave the highest naphthol yields, perhaps due to an allochemical effect.[6] The electron-rich **4** gave excellent yields of the naphthol. Dotz reported that reaction of the unsymmetrical carbene complex $(CO)_5Cr{=}C(p\text{-}C_6H_4CH_3)p\text{-}C_6H_4CF_3$ with diphenylacetylene produced the naphthol which resulted from annulation onto the electron-poor ring,[17] which led us to predict **3** to be superior. A low yield of one naphthol (none of the ipso substitution product was detected) was obtained from **2a**; the major product (20% yield) was the vinylketene methanolysis product, which may have formed through an ester cleavage of the alkyne or through quenching of an intermediate ketene complex during product isolation. The energy barrier to benzannulation prevents the intermediate vinylketene complex from cyclizing. Only the sterically favored naphthol resulting from benzannulation of **3** at the para position was isolated.

Attempts to determine the regioselectivity of the iron carbene complex benzannulation resulted in the finding that furans were

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(1) Portions of this work were presented at the 203rd National Meeting of the American Chemical Society in San Francisco, CA, Spring, 1992, as ORGN 0267.

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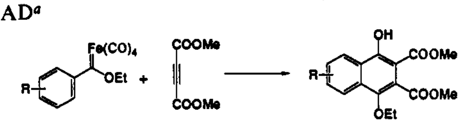
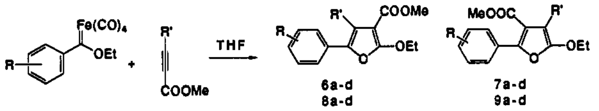
Table I. Benzannulation Reactions of Iron(0) Carbene Complexes with DMAD[a]



complex	R	naphthol	R	yield (%)	trimer (%)
1	H	**5a**	H	21	9
2a	2-OMe	**5b**	8-OMe	5	5
3	3-OMe	**5c**	7-OMe	33	2
4	4-OMe	**5d**	6-OMe	93	<1

[a] Yields represent the isolated yields of purified products.

Table II. Furan Formation from Reaction of Iron(0) Carbene Complexes with Methyl Propynoate or Methyl But-2-ynoate[a]



complex	R′	furan	yield (%)	furan	yield (%)	trimer (%)
1	H	**6a**	15	**7a**	4	17
1	Me	**8a**	25	**9a**	42	12
2a	H	**6b**	78	**7b**		
2a	Me	**8b**		**9b**	79	6
3	H	**6c**	22	**7c**	1	7
3	Me	**8c**	30	**9c**	19	
4	H	**6d**	42	**7d**	11	19
4	Me	**8d**		**9d**	80	8

[a] Yields represent isolated yields of purified products.

the major products (Table II). Neither pyrone complexes nor indenes were detected. Traces of naphthols were detected (^1H NMR at ca. 12 ppm). High yields (ca. 80%) of furan were obtained with **2a** and **4**. The regioselectivity of alkyne incorporation, which was established by chemical shift and NOE experiments, is consistent with steric rather than electronic control. The smaller end of the alkyne is incorporated closer to the carbene carbon. The alkyne cyclotrimers[18] were minor side products.

The mechanism of cyclization may involve the formation of a vinylcarbene complex[19] which undergoes CO insertion to form a vinylketene complex (then benzannulation) or an ethoxy migration to form the precursor to furan formation.[20] Rhodium- or copper-catalyzed conversions of cyclopropene carboxylates to pyrones, furans, oxepins, or phenols are believed to occur through similar intermediates.[21]

Iron(0) carbene complexes react with DMAD to form naphthols and with alkyne monoesters to form furans. The source of this unexpected selectivity is currently under investigation.

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Supplementary Material Available: Experimental procedures and full characterization data for all reported compounds (16 pages). Ordering information is given on any current masthead page.

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