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REACTION OF ARYL CHROMIUM CARBENE COMPLEXES WITH 1-HEXYNE; FORMATION OF UNUSUAL DIELS-ALDER CYCLOADDITION PRODUCTS

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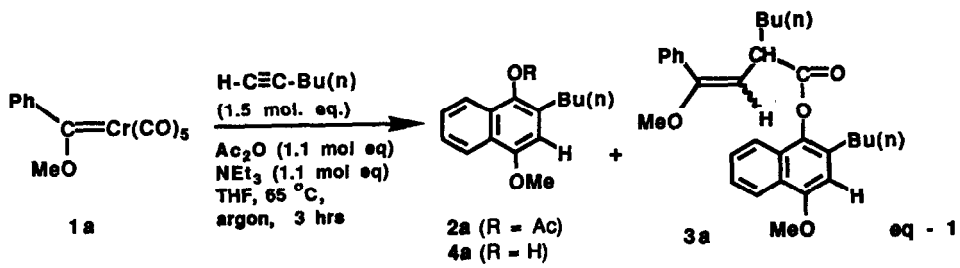
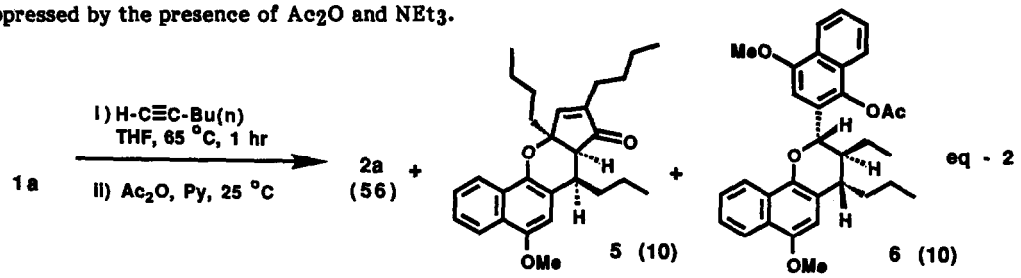
Abstract: The reaction of an aryl chromium carbene complex with 1-hexyne provided a benzannulated product as a major component along with unusual Diels-Alder cycloaddition products.

The reaction between the phenyl chromium carbene complex (**1a**) and an alkyne is a direct method for preparation of 1,4-dihydronaphthoquinone (**4a**),[1] and its mechanism has been studied extensively.[2] Although the naphthol (**4a**) is obtained as a major product from this type of reaction, several minor components and their mechanism of formation have not been fully characterized yet. We have observed that the reaction of **1a** with 1-hexyne under the conditions for *in situ* protection[3] provided the acetylated naphthol (**2a**) along with the vinyl ether derivative (**3a**), while the same reaction without *in situ* protection formed the free naphthol (**4a**) and interesting Diels-Alder cycloaddition products (**5** and **6**). In this paper, we report formation of the unusual by-products from the carbene-alkyne cycloaddition as well as mechanistic aspects for the formation of these structures.

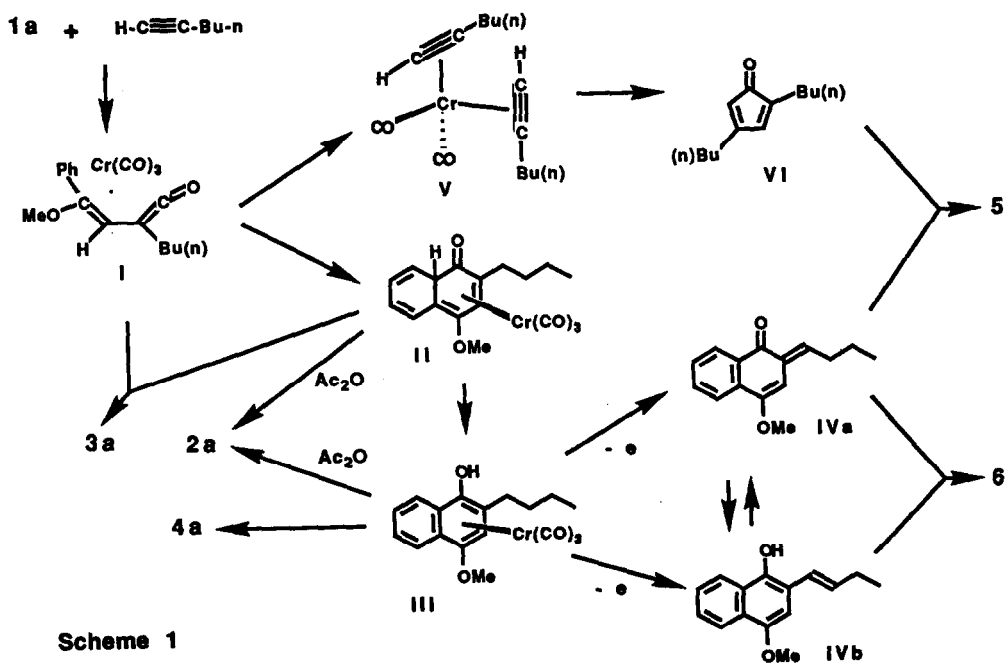


The reaction of **1a** with 1-hexyne (1.5 mol eq) in tetrahydrofuran (THF) at 65°C under argon in the presence of acetic anhydride (Ac_2O, 1.1 mol eq) and triethylamine (NEt_3, 1.1 mol eq) was complete in 3 hrs, providing **2a** (65%) and **3a** (18%), respectively (eq-1). On the other hand, the same reaction without Ac_2O and NEt_3, which was followed by acetylation (Ac_2O, pyridine), produced **2a** (56%) along with the

cyclopentanone adduct (**5**, 10%)[4] and the dimeric structure (**6**, 10%)[4], respectively (eq-2). No evidence of formation of **5** and **6** was observed from the reaction which was carried out under the *in situ* protection conditions. The structures **5** and **6** suggest the possible involvement of benzylic oxidation of the cycloaddition product (**4a**) and generation of the cyclopentadienone during the process, which was suppressed by the presence of Ac_2O and NEt_3.

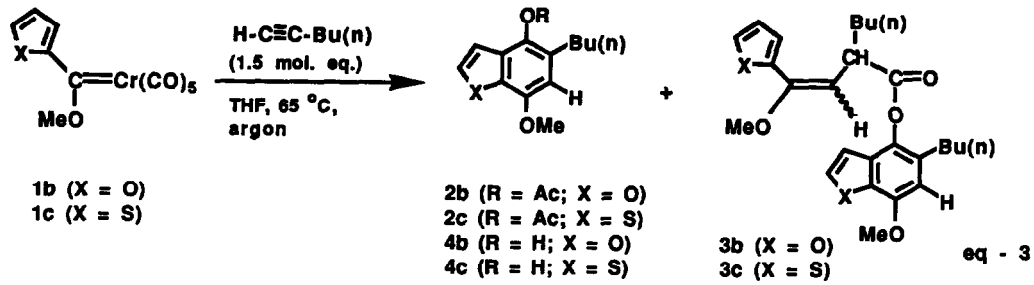


A plausible pathway for formation of **2a**, **3a**, **5** and **6** is outlined in Scheme 1. According to the previously proposed mechanism,[2] the reaction of **1a** and the alkyne produces the vinyl ketene complex of chromium (I). The 1,6-cycloaddition from I generates the cyclohexadiene intermediate (II), which is rapidly acetylated during aromatization.[3] The uncyclized vinyl ketene (I) would also serve as an acetylating agent for II, generating **3a**. Without Ac_2O and NEt_3, II aromatizes by a proton shift to form the free phenol (III). Alternatively, nucleophilic attack at the ketene carbon of I by III could produce **3a**.[5] The benzylic oxidation of III, probably accelerated by chromium tricarbonyl coordinating to the arene ring, would produce the transient ortho-quinone methide (**IVa**), which would isomeryze to the styryl intermediate (**IVb**).[6] Then, Diels-Alder cycloaddition between **IVa** and **IVb** could lead to the observed dimer structure (**6**). On the other hand, the vinyl ketene ligand might be replaced by an excess



Scheme 1

of (or unreacted) alkyne, generating a novel bis(alkyne)dicarbonylchromium complexes (V) originated from the carbonylmetal fragment.[7] Unusual carbonylation during the two-alkyne dimerization could produce the cyclopentadienone (VI), which then reacts with IVa, providing the observed cycloaddition product (5). Competition which exists between *in situ* acetylation of II by Ac_2O and by I as well as nucleophilic attack at the ketene carbon of the uncyclized I by the cyclized III may be governed by the strength of the acetylation reagents and nucleophilicity of the aryl group for 1,6-cycloaddition. In order to increase the acetylating power, addition of 4-dimethylaminopyridine (4-DMAP, 0.09 mol eq) with Ac_2O (2.2 mol eq) and NEt_3 (1.1 mol eq) decreased formation of **3a** to 4%. No further reduction of formation of **3a** was observed upon further increase in the amount of Ac_2O and 4-DMAP.



1b (X = O)
1c (X = S)

2b (R = Ac; X = O)
2c (R = Ac; X = S)
4b (R = H; X = O)
4c (R = H; X = S)

3b (X = O)
3c (X = S)

eq - 3

Table 1

Conditions	Products (isolated yield;%)
X = O : with Ac_2O, NEt_3, 24 hr	2b (68)
without Ac_2O, NEt_3, 20hr	4b (33) + 3b (35)
X = S : with Ac_2O, NEt_3, 24 hr	2c (66)
without Ac_2O, NEt_3, 20hr	4c (33) + 3c (10)

The vinyl ether formation considerably increased with the complex where the aryl group is more nucleophilic, such as furan (1b) and thiophene (1c) (eq 3). As shown in Table 1, the reaction of 1b with 1-hexyne (1.5 mol eq) in THF in the presence of 1.1 mol eq each of Ac_2O and NEt_3 took 24 hrs for completion, giving the acetate derivative (2b) in 68% yield. However, the same reaction without Ac_2O and NEt_3 resulted in formation of a 35% yield of the vinyl ether (3b) along with lesser yield (33%) of the benzannulated product (4b). These results indicate that the presence of Ac_2O and NEt_3 could be more than just *in situ* acetylating agents, possibly catalyzing this type of the reaction. Further studies regarding the roles Ac_2O and NEt_3 in this process are currently being investigated, and will be reported in due course.

References:

1. a) K.H. Dötz, *Angew. Chem. Int. Ed.*, **14**, 644 (1975); b) W.D. Wulff, P-C. Tang, K-S. Chan, J.S. McCallum, D.C. Yang and S.R. Gilbertson, *Tetrahedron*, **41**, 5813 (1985); c) M.F. Semmelhack, J.J. Bozell, L. Keller, T. Sato, E.J. Spiess, W.D. Wulff and A. Zask, *Tetrahedron*, **42**, 5803 (1985) and references therein.