ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 3, pp. 506–507. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.S. Zavgorodnii, M.G. Karpov, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 3, pp. 514–515.

LETTERS TO THE EDITOR

ortho-Effect of Hexacarbonyldicobaltacetylene Substituents of Propargyl Type in Aromatic Systems

V. S. Zavgorodnii and M. G. Karpov

St. Petersburg State Technological Institute, Moskovskii pr. 26, Saint-Petersburg, 190013 Russia
e-mail: v.zavg@yandex.ru

Received January 16, 2012

DOI: 10.1134/S1070363212030243

In this work we analyzed the features of cobalt-propargylation of some aromatic systems (ferrocene, five-membered nitrogen-containing heterocycles, thiophenes) with μ,η^2-hexa-carbonyldicobalt complexes of acetylenic alcohols of the propargyl type.

The cobalt-propargylation reaction proceeds under the influence of μ,η^2- hexacarbonyldicobalt complexes of acetylene alcohols of the propargyl structure in the presence of boron trifluoride diethyl etherate. The latter generates *in situ* a superstable carbenium cation $Co_2(CO)_6(R)C{\equiv}CC^+(R_2)$, where R are hydrogen atoms or different organic substituents. Such cations are sufficiently active electrophilic reagents [1–3].

It has been shown [2] that the μ,η^2-hexacarbonyldicobalt-2-propynol complex **I** reacts with ferrocene in the presence of $BF_3{\cdot}OEt_2$ to form the ferrocene derivative monosubstituted in the cyclopentadiene ring. With a four-fold excess of this complex the cobaltpropargylation occurs also in the second cyclopentadienyl ring to give the disubstituted product in a low yield.

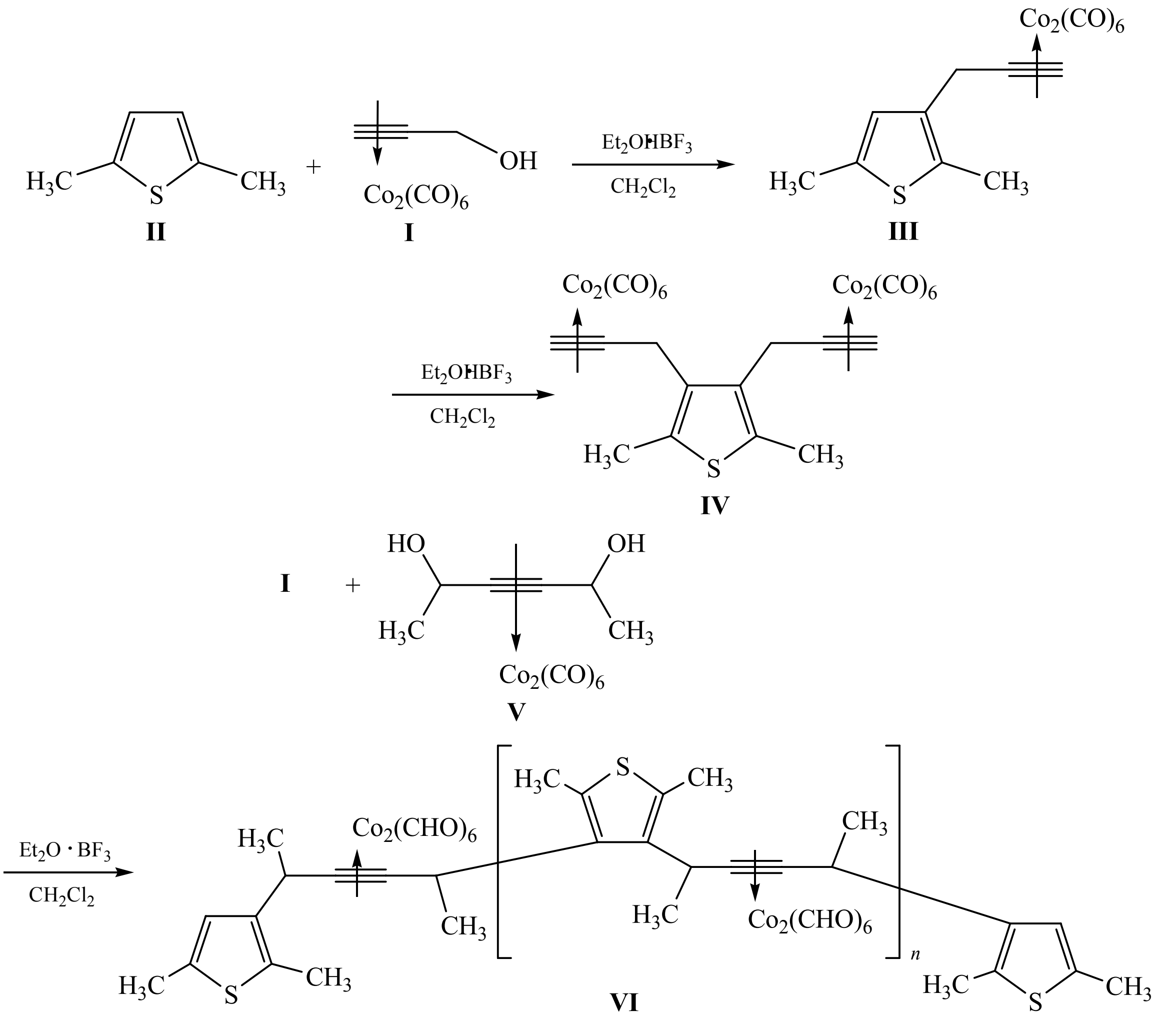
The carbazole is cobalt-propargylated with propynol complex **I** primarily at the HN nitrogen atom followed by substituting at the atoms C^3 and C^6 of carbazole skeleton [4]. The progenitor compound, pyrrole, is cobalt-propargylated with this complex on the α-carbon atom to form 2-(μ,η^2-hexacarbonyldicobalt-2-propynyl)pyrrole [3]. An attempt to introduce the second hexacarbonyldicobalt moiety into HN-position failed, although the cationic character of the reagent formed in the presence of $BF_3{\cdot}OEt_2$ from the complex **I** did not exclude such a possibility.

1,2,4-Triazole reacts with the propynol complex **I** exclusively at the nitrogen atom HN^1 to give 1-(μ,η^2-hexacarbonyldicobalt-2-propynyl)-1,2,4-triazole [3]. The subsequent cobaltpropargylation also does not proceed, despite the fact that the electron density on the C^5 atom should remain sufficient for the electrophilic attack on it.

The *C*-substituted tetrazoles are cobaltpropargylated at the nitrogen atoms N^1 or N^2 to form primarily the N^2-monosubstituted products [3]. The unsubstituted 1*H*-tetrazole gives one *N*-cobaltpropargylated product, whose assignment to the N^1- or N^2-substitution is impossible. However, *N*,*N*-bis(μ,η^2-hexacarbonyldicobalt-2-propynyl)carbamide was detected as a byproduct [3]. Its formation can be represented as the result of biscobaltpropargylation of tetrazole on the N^1- and N^4-positions, followed by the oxidative degradation of the ring, which loses aromaticity due to the introduc-tion of the second cobaltpropargyl moiety into the ring.

This analysis may indicate the benefit of the *ortho*-effect of cobaltpropargyl substituent preventing the entry of the second cobaltpropargyl moiety into the *ortho*-position relative to the just entered one. Obviously, in the examined aromatic systems this substituent exhibits a deactivating effect in subsequent reactions of electrophilic substitution, manifesting the electron-withdrawing properties (in the case of the ferrocene cobaltpropargylation) and providing the steric hindrances (in the cases of the five-membered nitrogen-containing compounds).

Continuing this research, we studied the cobalt-propargylation of thiophenes. The unsubstituted thiophenes are cobaltpropargylated with propynol complex **I** only at 2 and 5 positions, but the introduction of the second moiety is much more difficult and low-productive even in the presence of 4-fold excess of the



complex **I**. The subsequent cobaltpropargylation of biscobalt-substituted thiophene is not occurring.

In the case of 2,5-dimethylthiophene **II**, containing only reactive β-positions [5], the reaction in the presence of cobaltpropargylating agent excess at a significant increase in the contact time of the reagents (in comparison with the formation of monosubstituted product) results in 3,4-disubstituted product **IV**. Note that the reaction of 2,4-biscobaltpropargylation of dimethylthiophene occurs with both the propynol complex **I** and 3-hexyn-2,5-diol **V** having a more bulky substituent.

The structure of compounds **III**, **IV**, and **VI** was confirmed by the spectral methods. These data and experimental details will be published elsewhere.

Thus, the *ortho*-effect of cobaltpropargyl substituent in the electrophilic cobaltpropargylation of aromatic compounds depends primarily on the enrichment of the latter with the electron density. If the electron density on the attacked atom is sufficient, this effect can be overcome in more rigid reaction conditions, which allows to obtain the *ortho*-disubstituted products.

REFERENCES

1. Lockwood, R.F. and Nicholas, K.M., *Tetrahedron Lett.*, 1977, p. 4163.
2. Denisov, V.R., Karpov, M.G., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 8, p. 1251.
3. Karpov, M.G., Zavgorodnii, V.S., Denisov, V.R., Ostrovskii, V.A., and Zubarev, V.Yu., *Zh. Org. Khim.*, 2001, vol. 37, no. 8, p. 1194.
4. Karpov, M.G., Zavgorodnii, V.S., and Denisov, V.R., *Zh. Org. Khim.*, 2001, vol. 37, no. 12, p. 1812.
5. Bliks, F., *Geterotsiklicheskie soedineniya* (Heterocyclic Compounds), Moscow: Inostrannaya Literatura, 1953, vol. 1, p. 171.