

SHORT
COMMUNICATIONS

Metallopropargylation of Five-membered NH-Containing Heterocycles with Hexacarbonyldicobalt-1-propynol*

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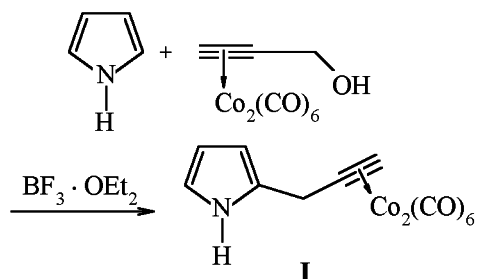
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The applicability of generated *in situ* hexacarbonyldicobaltpropargyl carbocations for metallopropargylation of aromatic compounds [1], ferrocene [2] and a number of other type compounds, in particular, indole and tryptamine derivatives [3] was demonstrated formerly. Therewith indole with hexacarbonyldicobalt-1,1-dimethyl-2-propynol afforded predominantly the product of β -C-cobaltpropargylation and a little of a substance bis-cobaltpropargylated at carbon and nitrogen atoms.

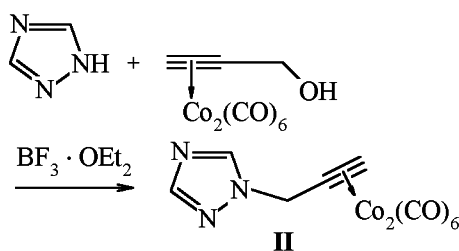
Here we report on results of reactions between hexacarbonyldicobaltpropynol with five-membered aromatic heterocycles. The reactions with all compounds under study were carried out in the presence of boron trifluoride etherate in dichloromethane at room temperature. They were completed within several minutes after mixing the components.

Pyrrole underwent metallopropargylation nearly exclusively at the α -carbon of the ring.



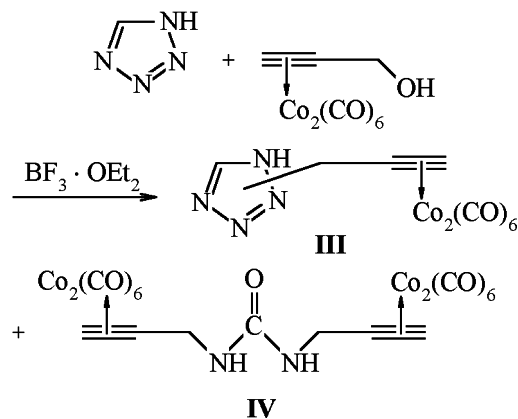
Unlike pyrrole the triazoles and tetrazoles we used afforded the products of NH-substitution. 1,2,4-Triazole underwent metallopropargylation exclusively in 1 position.

In the ¹H NMR spectrum of the reaction product are present two signals of equal intensity from the



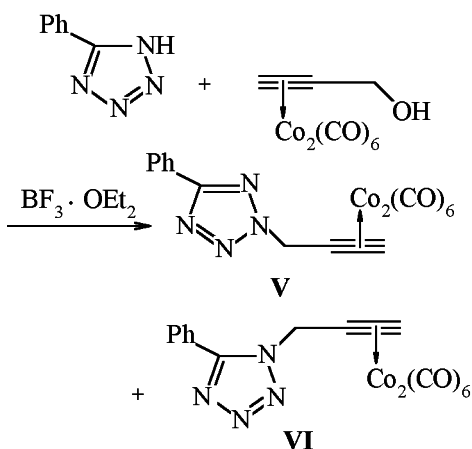
protons attached to carbons of the ring indicating the nonequivalence of C³ and C⁵ atoms; thus the alternative structure with a substituent at N⁴ is excluded.

With tetrazole we obtained a single product of N-metallopropargylation that we failed to assign to N¹ or N² isomer. A side product, N,N'-bis(μ, η^2 -hexacarbonyldicobalt-2-propynyl)carbamide, arose due to decomposition of dialkylation product at N¹ and N⁴ positions in the tetrazole ring.



In 5-phenyltetrazole prevails the substitution in position 2; also forms some product of replacement in position 1 (up to 10%).

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All the complexes we prepared I–V are stable liquid or crystalline substances of bright red color (dark-red in solutions). The compounds are readily identified by TLC and are easily isolated by chromatography on silica gel (eluent hexane–ether). Therefore their formation may be used for analytical purposes and for synthesis of pure compounds by demetallation effected with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. In this process the propargyl structure of the substituent and its position in the ring is conserved.

Metallopropargylation of NH-containing heterocycles. To a solution or dispersion of 1.1 mmol of azole and 1 mmol of hexacarbonyldicobaltpropynol in 20 ml of anhydrous CH_2Cl_2 was added dropwise at 18–20°C a slight excess of boron trifluoride etherate. Insoluble azoles dissolved in the course of the reaction. After addition of the boron trifluoride etherate was finished the mixture was left standing for 10–20 min, and then diluted with an equal volume of water. The organic layer was separated, dried on Na_2SO_4 for 20–30 min, CH_2Cl_2 was distilled off, and the product was purified by chromatography on a column packed with silica gel, eluent hexane–ether. On removing the solvent virtually pure compounds were obtained.

Removing of cobalt protection. To a solution of 0.1 mmol of complex V in ethanol at 40–50°C was added at stirring a solution of 1 mmol of $\text{Fe}(\text{NO}_3)_3$ hydrate in ethanol, and the mixture was maintained till the end of gas liberation. Therewith abundant flakes of precipitate separated. The reaction was monitored by TLC. The ethanol was distilled off, the residue was diluted with CHCl_3 , and the solution was filtered through a thin silica gel bed. On removing the solvent pure compound was obtained. The formation of solely 2-(2-propynyl)-5-phenyltetrazole suggests that no migration of the triple bond occurs during demetallation, and the position of the propargyl

substituent is conserved, for the shift of the substituent should have resulted in formation of allene and acetylene isomers.

The structure of compounds obtained was confirmed by ^1H NMR spectra. The spectra were registered on Bruker AC-200 instrument at operating frequency 200 MHz (CDCl_3). We failed to perform the elemental analysis of hexacarbonyldicobalt derivatives for they decarbonylated under the conditions of analysis.

2-(μ, η^2 -Hexacarbonyldicobalt-2-propynyl)-pyrrole (I). Dark-red oily substance. ^1H NMR spectrum, δ , ppm: 4.10 s (2H, CH_2), 6.04 s (2H, C^3H), 6.10 s (1H, $\text{HC}\equiv$), 6.68 s (1H, C^2H), 8.09 s (1H, NH).

1-(μ, η^2 -Hexacarbonyldicobalt-2-propynyl)-1,2,4-triazole (II). Dark-red crystals, $T_{\text{decomp}} > 11^\circ\text{C}$. ^1H NMR spectrum, δ , ppm: 5.45 s (2H, CH_2), 6.10 s (1H, $\text{HC}\equiv$), 8.09 s (1H, C^5H), 8.32 s (1H, C^3H).

1-(μ, η^2 -Hexacarbonyldicobalt-2-propynyl)tetrazole (III). Dark-red crystalline substance, decomposes at heating. ^1H NMR spectrum, δ , ppm: 5.27 s (2H, CH_2), 6.15 s (1H, $\text{HC}\equiv$), 7.52 s (1H, C^5H).

***N, N'*-Bis(μ, η^2 -hexacarbonyldicobalt-2-propynyl)carbamide (IV).** Dark-red crystalline substance, decomposes at heating. ^1H NMR spectrum, δ , ppm: 4.58 d (4H, CH_2 , J 2.5 Hz), 4.7 t (2H, NH, J 6 Hz), 6.07 s (2H, $\text{HC}\equiv$).

2-(μ, η^2 -Hexacarbonyldicobalt-2-propynyl)-5-phenyltetrazole (V). Bright red crystals, mp 50–52°C. ^1H NMR spectrum, δ , ppm: 5.91 s (2H, CH_2), 6.17 s (1H, $\text{HC}\equiv$), 7.46 s (3H, ArH), 8.16 s (2H, ArH).

1-(μ, η^2 -Hexacarbonyldicobalt-2-propynyl)-5-phenyltetrazole (VI). Red crystals, mp 92–94°C. ^1H NMR spectrum, δ , ppm: 5.94 s (1H, $\text{HC}\equiv$), 5.80 s (2H, CH_2), 7.58 s (2H, ArH), 7.73 s (3H, ArH).

2-(2-Propynyl)-5-phenyltetrazole. Colorless oily substance. ^1H NMR spectrum, δ , ppm: 2.4 t (1H, $\text{HC}\equiv$, J 2.5 Hz), 5.30 d (2H, CH_2 , J 2.5 Hz), 7.32 m (3H, ArH), 8.03 m (2H, ArH).

REFERENCES

- Lockwood, R.F. and Nicolas, K.M., *Tetrahedron Lett.*, 1977, pp. 4163–4165.
- Denisov, V.R., Karpov, M.G., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 8, pp. 1251–1252.
- Nakagawa, M., Ma, J., and Hino, T., *Heterocycles*, 1990, vol. 30, no. 1, pp. 451–462.