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Reactions of Carbazoles with Hexacarbonyl Dicobalt Complexes of Propynol and 1,4-Butynediol*

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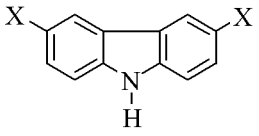
Abstract—Metallopropargylation of a number of carbazoles was performed by dicobalt hexacarbonyl complexes with propargyl alcohol and 1,4-butynediol in the presence of boron trifluoride etherate. It was shown that depending on the substituents position in the carbazole ring occurred either N- of C-propargylation; with 1,4-butynediol formed also oligomeric products.

Propargyl derivatives of carbazoles attract attention as potential monomers for production of materials with unique properties [1]. However the published procedures concern only preparation of N-carbazoles [2, 3] that arise in mixtures with allene isomers. It is known that μ,η^2-complexes of dicobalt hexacarbonyl with propargyl alcohols treated with acid reagents readily generate a complex propargyl carbocation possessing electrophilic properties. We studied the reactivity of the above complexes toward five-membered heterocycles and established [5] that μ,η-hexacarbonyldicobaltopropynol (**I**) with pyrrole provided a product of C-propargylation, 2-(μ,η^2-hexacarbonyldicobalto-2-propynyl)pyrrole. The NH-containing triazoles and tetrazoles are metallopropargylated exclusively at the nitrogen atom affording 3-(*N*-heteryl)-μ,η^2-hexacarbonyldicobalto-1-propynes. The latter after elimination of cobalt protection afford the corresponding propargylated derivatives with no allene isomers.

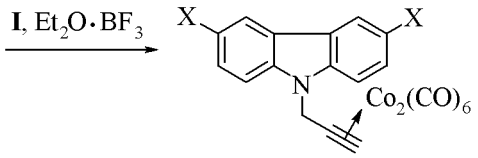
In the present communication we report on the results of the metallopropargylation of a number of carbazoles with complex (**I**) and with μ,η^2-hexacarbonyldicobalto-1,4-butynediol (**II**).

Unsubstituted carbazole (**III**) and 3,6-dibromocarbazole (**IV**) in the presence of boron trifluoride etherate undergo metallopropargylation first of all at the nitrogen atom to yield 9-(μ,η^2-hexacarbonyldicobalto-2-propynyl)carbazole (**V**) and 3,6-dibromo-9-(μ,η^2-hexacarbonyldicobalto-2-propynyl)carbazole (**VI**) respectively.

With both compounds the substitution at the nitrogen atom completes at room temperature in several minutes.



III, IV



V, VI

X = H (**III, V**), Br (**IV, VI**).

N-substituted carbazoles, 9-methylcarbazole (**VII**) and 9-metallopropargylated carbazole (**V**), under the action of complex **I** suffer C-metallopropargylation into *3* and *6* positions.

The reaction occurs consecutively and does not stop at mono C-substituted product. The final products are trisubstituted carbazoles **VIII** and **IX** (see Scheme).

The C-metallopropargylation rate is a lot slower than that of the N-metallopropargylation. The rate of compound **IX** formation is somewhat less than that of compound **VIII**. This means that the electron-donor effect on the carbazole ring produced by hexacarbonyldicobaltopropargyl substituent is less than that of the methyl group.

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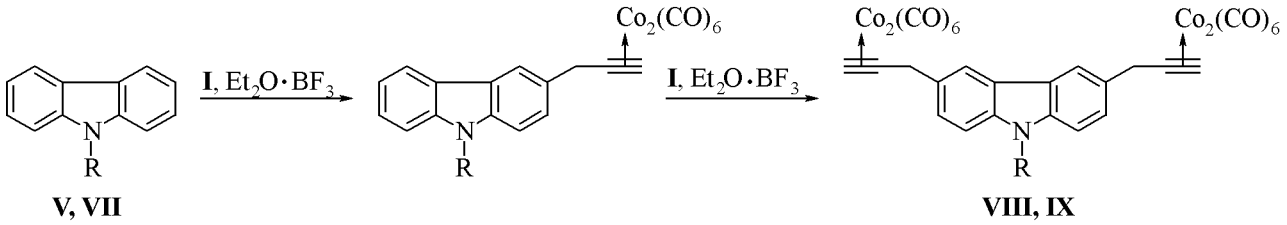
Scheme.

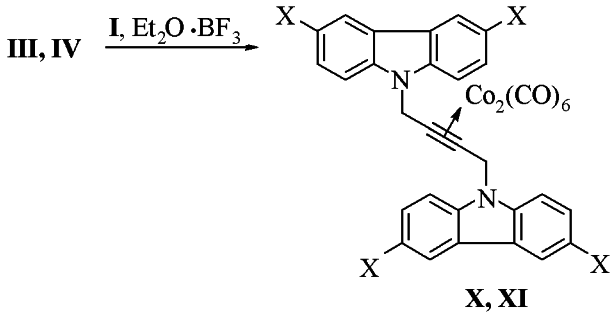


V, VII **VIII, IX**

R = CH_3 (**VII, VIII**), μ,η^2-hexacarbonyldicobalto-2-propynyl (**V, IX**).

N-Metallopropargylated complexes **V** and **VI** are considerably more stable against heating and air oxygen both in crystalline state and in solution than the C-metallopropargylated products **VIII** and **IX**. This is presumably due to electron-acceptor effect of nitrogen on the metallopropargyl group. It is indirectly supported by the downfield shift of the methylene protons of the propargyl moiety in the ^{1}H NMR spectra of compounds **V** and **VI** as compared with the signal of the same group in the spectrum of compound **VIII**.

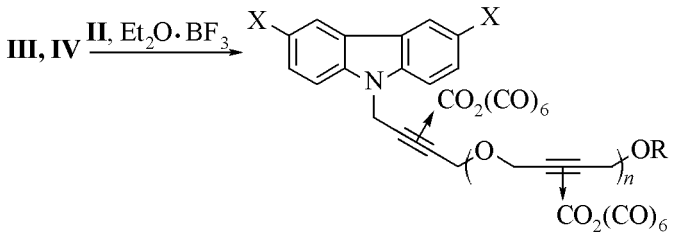
The reaction of complex diol **II** with carbazoles **III** or **IV** gives a single product, 1,4-bis(9-carbazolyl)-$\mu\eta^2$-hexacarbonyldicobalto-2-butyne (**X**) and 1,4-bis(3,6-dibromo-9-carbazolyl)-$\mu\eta^2$-hexacarbonyldicobalto-2-butyne (**XI**) respectively, only when excess carbazole is used.



X, XI

X = H (**X**), Br (**XI**).

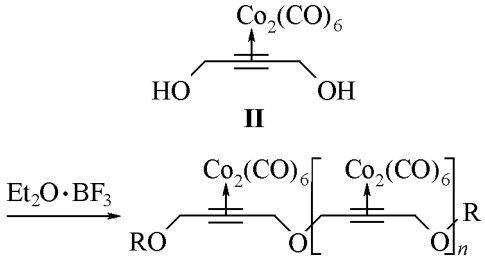
At excess diol complex **II** according to TLC data arises an inseparable mixture of polyethers **XII** and **XIII**



XII, XIII

X = H (**XII**), Br (**XIII**); R = H, Et.

This fact is due to reaction at the beginning of the process in dichloromethane between complex **II** and boron trifluoride etherate resulting in complexes of oligomeric butynediol ethers and mixed ethyl butynediol ethers that behave as propargylating agents.



II

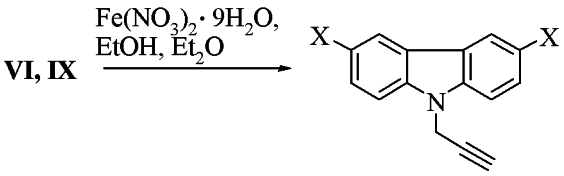
R = H, Et.

The electrophilic metallopropargylation requires excess of boron trifluoride etherate. The composition of the reaction mixture in this case would apparently be largely governed by the solubility both of the initial polyethers and the final reaction products.

As shows TLC monitoring the reaction between excess 9-methylcarbazole (**VII**) and complex diol **II** proceeds through a number of intermediate products and results by formation of a complex of disubstituted butyne **XIV** that contains according to ^{1}H NMR spectrum some oligomers **XV** as impurity.

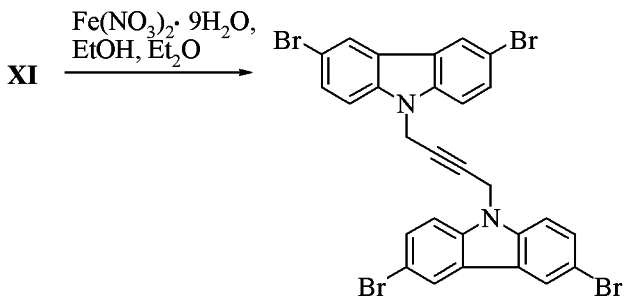
The complexes of 9-propargylcarbazoles, also those substituted in *3* and *6* positions, unlike the initial NH-carbazoles are well soluble in low-polar solvents and are of intense color that significantly facilitates their analysis and chromatographic separation on silica gel. Besides the mass spectra of the propargylcarbazole complexes are easier for interpretation than those of the original NH-carbazoles. The characteristic fragmentation features of the complexes under the electron impact and the ease of their synthesis provides a tool for the study of the initial NH-carbazole structure.

The $Co_2(CO)_6$ moiety is easily eliminated by the action of mild oxidizers. We demonstrated this by an example of compounds **VI**, **IX**, and **XI**.



XVI, XVII

X = Br (**XVI**), HC≡CCH$_2$ (**XVII**).



XVIII

Complexes **VI** and **XI** with the metallopropargyl substituent only at nitrogen of the heterocycle undergo demetallation more cleanly affording in high yield products **XVI** and **XVIII** respectively. The homogeneity of compound **XVI** was confirmed by TLC on silica gel (eluent chloroform), and the assumed structure is consistent with the ^{1}H NMR spectrum. Besides the IR spectrum of the compound lacks absorption bands characteristic of allenes in the 1960–2000 cm $^{-1}$ region, and the narrow band of medium intensity at 3320 cm^{-1} shows the presence of a terminal triple bond. Compound **XVIII** is virtually insoluble at room temperature in most solvents and thus it cannot be purified by TLC and column chromatography. However recrystallization of amorphous powdery compound **XVIII** from boiling DMF provides the substance with negligible losses as colorless uniform crystals melting in a narrow temperature range without decomposition. Thus the compound was also obtained in an individual state. The elemental analysis corresponds to an empirical formula of 1,4-bis(3,6-dibromo-9-carbazolyl)-2-butyne (**XVIII**). In its ^{1}H NMR spectrum appear the signals characteristic of the 3,6,9-substituted carbazole ring and of symmetrically substituted butyne.

Complex **IX** with three substituent at the carbazole ring containing $Co_2(CO)_6$ moiety also underwent complete demetallation forming predominantly compound **XVII** and a little (15%) of compound with unestablished structure. TLC on silica gel provided a possibility to observe formation of several intermediate compounds of red color, presumably the products of successive elimination of $Co_2(CO)_6$ moieties. The ^{1}H NMR spectrum of compound **XVIII** confirms its structure, and the IR spectrum reveals that all the three substituents have propargyl and not allene structure.

EXPERIMENTAL

^{1}H NMR spectra of compounds **V, VI, VIII, IX, XI** dissolved in CCl_4 or $CDCl_3$ were registered on spectrometer Tesla BS 497 (100 MHz), of compounds **X, XIV, XVI, XVII** in $CDCl_3$ solutions on spectrometer Bruker C200 (200 MHz). Mass spectra were taken on MSD-650 instrument (electron impact, electrons energy 70 eV).

9-(μ,η^2-Hexacarbonyldicobalto-2-propynyl)-carbazole (V). To a solution of 0.35 g (2.1 mmol) of carbazole and 0.228 g (0.7 mmol) of propargyl alcohol complex **I** in 20 ml of anhydrous CH_2Cl_2 at room temperature was added 0.25 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 10 min and then diluted with 20 ml of water. The organic layer was separated and dried with Na_2SO_4. The product was isolated by column chromatography on silica gel, eluent hexane. We obtained 0.141 g (43%) of compound **V** as thin red needles. mp 118–119°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 5.7 s (2H, CH_2), 6.1 s (1H, ≡CH), 7.5 m (6H, H arom), 8.2 m (2H, H arom). Mass spectrum, *m/z* (I_{rel} , %): 463 (2) [*M*–CO]$^{+\cdot}$, 435 (2), 407 (8), 379 (4), 351 (11), 323 (15), 241 (10), 218 (8), 205 (100), 192 (27), 179 (39), 166 (99), 152 (25), 139 (63), 127 (11), 115 (42), 102 (15), 89 (24), 87 (13), 83 (28).

3,6-Dibromo-9-(μ,η^2-hexacarbonyldicobalto-2-propynyl)carbazole (VI). To a solution of 0.2 g (2.1 mmol) of 3,6-dibromocarbazole and 0.21 g (0.62 mmol) of complex **I** in 20 ml of anhydrous CH_2Cl_2 at room temperature was added 0.1 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 30 min and then worked out as described above. The reaction product was isolated by column chromatography on silica gel using as eluent a mixture hexane–dichloromethane, 5:1. We isolated 0.355 g (89%) of compound **VI** as red crystals. mp 102–103°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 5.3 s (2H, CH_2), 5.8 s (1H, ≡CH), 7.1 d [2H, H arom ($H^{1,8}$), *J* 8 Hz], 7.4 d [2H, H arom ($H^{2,7}$), *J* 8 Hz], 7.9 br.s (2H, H arom). Mass spectrum, *m/z* (I_{rel} , %): 621 (12) [*M*–CO]$^{+\cdot}$, 593 (13), 565 (100), 537 (12), 509 (10).

3,6-Bis(μ,η²-hexacarbonyldicobalto-2-propynyl)-9-methylcarbazole (VIII). To a solution of 0.08 g (0.44 mmol) of *N*-methylcarbazole and 0.4 g (1.17 mmol) of complex **I** in 5 ml of anhydrous CH_2Cl_2 at room temperature was added 0.5 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 1 h and then 2 ml of isooctane was added, and dichloromethane was evaporated in a vacuum. The solution (~2 ml) was separated from the tarry residue and applied to a chromatographic column charged with silica gel. Elution was performed with hexane to afford 0.35 g of red crystalline substance. On recrystallization from hexane we obtained 0.11 g of compound **VIII** as fine crystals. Yield 30%, mp 105–106°C (decomp). ^{1}H NMR spectrum, δ, ppm: 4.0 s (3H, CH_3), 4.4 s (4H, CH_2), 6.3 s (2H, ≡CH), 7.5 m (4H, H arom), 8.1 m (2H, H arom).

3,6,9-Tris(μ,η²-hexacarbonyldicobalto-2-propynyl)carbazole (IX). To a solution of 0.025 g (0.15 mmol) of carbazole and 0.25 g (0.73 mmol) of complex **I** in 20 ml of CH_2Cl_2 at room temperature was added 0.3 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 2 h, the solvent was distilled off, and 2 ml of hexane was added to the residue. The separated tarry substance was removed, and the solution was applied to a chromatographic column charged with silica gel. Elution was performed with hexane to afford 0.16 g of dark-red crystalline substance. On recrystallization compound **IX** was obtained as dark-red powder, yield 0.09 g (53%). The compound decomposes when heated over 145°C. ^{1}H NMR spectrum, δ, ppm: 4.4 br.s (4H, CH_2, metallopropargyl group in position *3*, *6*), 5.8 br.s (2H, CH_2, metallopropargyl group at nitrogen, 6.0 br.s (1H, metallopropargyl at nitrogen), 6.3 br.s (2H, ≡CH, metallopropargyl group in positions *3*, *6*), 7.5 m (4H, H arom), 8.1 br.s (2H, H arom).

1,4-Bis(9-carbazolyl)-μ,η²-hexacarbonyldicobalto-2-butyne (X). To a solution of 0.15 g (0.9 mmol) of carbazole and 0.05 g (0.13 mmol) of butynediol complex **II** in 20 ml of anhydrous CH_2Cl_2 at room temperature was added 0.2 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 10 min and then diluted with 20 ml of water. The organic layer was separated and dried with Na_2SO_4. The product was isolated by column chromatography on silica gel, eluent hexane–CH_2Cl_2. We obtained 0.02 g (22%) of compound **X** as bright red crystals. The compound decomposed at temperature over 250°C. ^{1}H NMR spectrum, δ, ppm: 5.50 s (4H, CH_2), 7.23 d.d [4H, H arom (H^3,H^4), J(H^3,H^4)⊂ ⊂J(H^2,H^3) 7.5 Hz], 7.28 d [4H, H arom (H^1), J 7.5 Hz], 7.43 d.d. [4H, H arom (H^2,H^3), J(H^2,H^3)⊂J(H^1,H^2) 7.5 Hz], 8.08 d [4H, H arom (H^4), J 8.4 Hz].

1,4-Bis(3,6-dibromo-9-carbazolyl)-μ,η²-hexacarbonyldicobalto-2-butyne (XI). To a solution of 0.2 g (0.62 mmol) of 3,6-dibromocarbazole and 0.1 g (0.27 mmol) of butynediol complex **II** in 30 ml of CH_2Cl_2 at room temperature was added 0.2 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 1 h and then diluted with 10 ml of water. The organic layer was separated and dried with Na_2SO_4. The product was isolated by column chromatography on silica gel, eluent petroleum ether–CH_2Cl_2. We obtained 0.16 g (60%) of compound **XI** as red crystals. The compound decomposed at heating over 170°C. ^{1}H NMR spectrum, δ, ppm: 5.3 s (4H, CH_2), 7.0 d (4H, H arom, ^3J 9 Hz), 7.5 d.d (4H, H arom, ^3J 9, ^4J 2 Hz), 8.0 d (4H, H arom, ^4J 2 Hz).

1,4-Bis(9-methyl-3-carbazolyl)-μ,η²-hexacarbonyldicobalto-2-butyne (XIV). To a solution of 0.36 g (2 mmol) of methylcarbazole and 0.25 g (0.67 mmol) of butynediol complex **II** in 25 ml of CH_2Cl_2 at room temperature was added 0.3 ml of $Et_2O{\cdot}BF_3$. The mixture was stirred for 3 h and then diluted with 20 ml of water. The organic layer was separated and dried with Na_2SO_4. The product was isolated by column chromatography on silica gel, eluent chloroform. We obtained 0.265 g of compound **XIV** contaminated by oligomers **XV** as dark-red oily substance. ^{1}H NMR spectrum, δ, ppm: 3.6–3.9 m (7.6H, CH_3), 4.0–4.3 m (7.1H, CH_2), 7.0–7.5 m (10H, H arom), 7.7–8.1 m (4.2H, H arom).

3,6-Dibromo-9-(2-propynyl)carbazole (XVI). To a solution of 0.33 g (0.5 mmol) of complex **VI** in 5 ml of EtOH was added threefold excess of alcoholic solution of $Fe(NO_3)_3 \times 9H_2O$. The mixture was heated to 50°C till gas evolution stopped. On cooling the reaction mixture was diluted with threefold volume of water. The separated precipitate was filtered off and washed on the filter with 5% HCl solution to remove the iron salts, then with water till neutral washings. After drying in air till constant weight we obtained 0.159 g of chromatographically pure amorphous compound **XVI**. Yield 96%. On recrystallization from chloroform were obtained colorless needle-like crystals, mp 196–198°C. Yield 96%. IR spectrum (1.5% solution in $CHCl_3$), ν, cm^{-1}: 3320 m, 2935 m, 2865 m, 1710 m, 1470 s, 1440 m, 1285 m, 1140 s, 740 s. ^{1}H NMR spectrum, δ, ppm: 2.28 t (1H, ≡CH, J 2 Hz), 4.97 d (2H, CH_2, J 2 Hz), 7.35 d (2H, H arom, J 9 Hz), 7.59 d (2H, H arom, J 9 Hz), 8.13 m (2H, H arom). Found, %: C 49.69,

49.52; H 2.27, 2.54. $C_{15}H_9Br_2N$. Calculated, %: C 49.58; H 2.48.

3,6,9-Tris(2-propynyl)carbazole (XVII). To a solution of 0.577 g (0.5 mmol) of complex **IX** in a mixture of 10 ml of EtOH and 20 ml of Et_2O was added at room temperature while stirring 5 g of $Fe(NO_3)_3 \times 9H_2O$ in 290ml of EtOH. The reaction mixture was left standing for 48 h, then 20 ml of hexane and 30 ml of water was added thereto. The organic layer was separated, washed with water (2×30 ml), and dried on Na_2SO_4. The dryer was separated, the solvent was evaporated in a vacuum, and the residue was dissolved in hexane and applied to a column charged with silica gel. By a hexane–dichloromethane mixture, 10 : 1, was first eluted compound **XVII**. Then occurred elution of the side product with a more polar system hexane–dichloromethane, 1 : 10. The monitoring was carried out by TLC on silica gel. After removing solvents from the respective fractions we obtained 0.02 g of compound **XVII** as very fine needle-like colorless crystals, mp 131–132°C, and 0.004 g of unidentified colorless oily substance that became yellowish on standing in air. IR spectrum (CCl_4), ν, cm^{-1}: 3330 m, 2870–2970 m, 1130 s, 630 m. ^1H NMR spectrum, δ, ppm: 2.3 br.s (3H, ≡CH), 3.73 br.s (4H, CH_2), 5.02 br.s (2H, CH_2), 7.39 m (2H, H arom), 7.47 m (4H, H arom), 8.04 s (2H, H arom). Found, %: C 90.02, 89.51; H 5.06, 5.29. $C_{21}H_{15}N$. Calculated, %: C 89.63; H 5.35.

1,4-Bis(3,6-dibromo-9-carbazolyl)-2-butyne (XVIII). The $Co(CO)_6$ group was removed as described for compound **XVI**. After recrystallization from DMF the demetallation product **XVIII** was obtained in nearly quantitative yield as small colorless pellets of mp 318–320°C. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.29 m (2H, CH_2), 7.53 m (4H, H arom), 8.46 m (2H, H arom). Found, %: C 48.91, 47.83; H 2.31, 2.40. $C_{28}H_{16}Br_4N_2$. Calculated, %: C 48.0; H 2.4.

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