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Copper and Copper Oxides Nanopowders in the Oxidative Condensations of Phenylacetylene and *tert*-Butylacetylene

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Abstract—Transformations of phenylacetylene and *tert*-butylacetylene in the presence of copper and copper oxide (Cu_2O, CuO) nanopowders prepared by gas-phase condensation of copper in argon were studied. The reaction of phenylacetylene with copper oxide nanopowders having different phase compositions in the absence of a solvent at room temperature resulted in oxidative condensation of phenylacetylene and complex formation of the condensation product. The complex undergoes decomposition by the action of acids, bases, and compounds capable of forming complexes. According to the X-ray diffraction data, one of the products is a new "parquet" modification of diphenyldiacetylene. Under analogous conditions, *tert*-butylacetylene gave rise to a complex mixture of products among which di-*tert*-butyldiacetylene was identified by gas chromatography–mass spectrometry. No copper complexes with the *tert*-butylacetylene condensation products were detected.

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In the past decade, data have been published on prospects in using nanostructured metals and metal oxides in organic synthesis due to their specific mechanical, optical, electric, magnetic, and chemical properties that differ from the properties of the corresponding macroparticles. However, available information on organic reactions involving nanocrystalline metals and their oxides is very scanty [1]. Therefore, the use in organic synthesis of nanocrystalline copper and copper oxides prepared by condensation of the metal vapor from an inert gas containing a controlled amount of oxygen attracts a certain interest [2].

In the present work we examined reactions of phenylacetylene (**I**) and *tert*-butylacetylene with copper and copper oxide (Cu_2O, CuO) nanopowders. It is known that acetylenic hydrocarbons in the presence of metals and their oxides and salts undergo oxidative condensation which underlies a general method for the synthesis of long-chain unsaturated hydrocarbons with a system of conjugated triple and double bonds. For example, monosubstituted acetylenes react with $Ni(PCl_3)_4$ to give complex mixtures of acyclic compounds having conjugated double and triple bonds, as well as aromatic and nonaromatic cyclic compounds (e.g., benzene and cyclooctatetraene derivatives) [3].

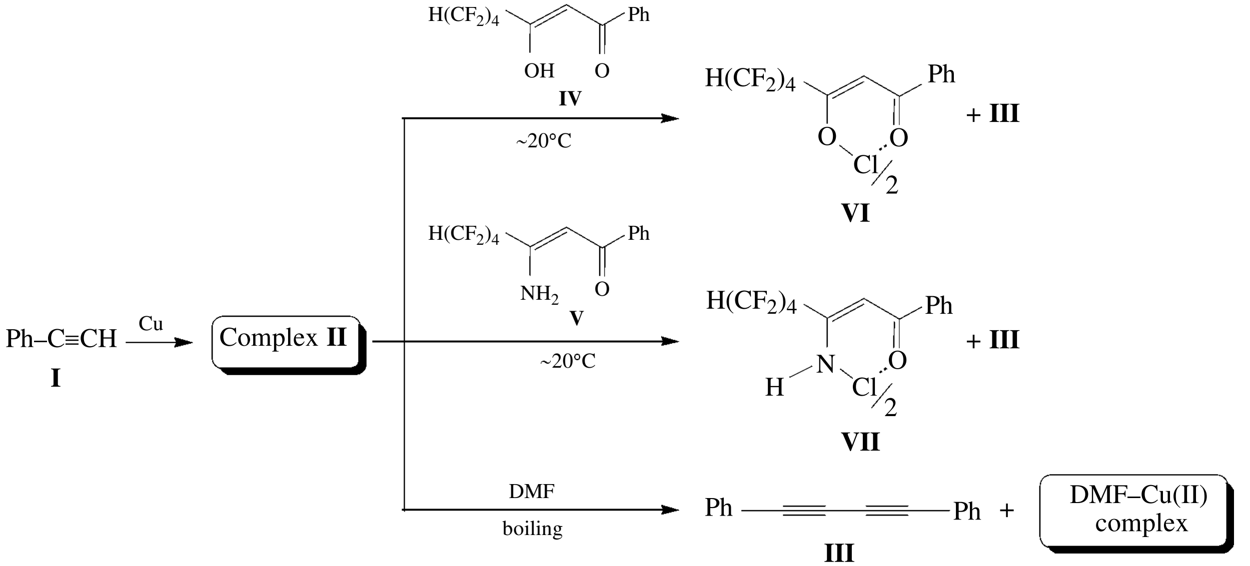
Treatment of phenylacetylene (**I**) with nanopowders having different phase compositions without a solvent at room temperature promoted its oxidative condensation and complex formation of the condensation product to give yellow powder **II**. The data of X-ray phase analysis showed the absence of copper or its oxides in the product. Apart from compound **II**, diphenyldiacetylene was detected in the reaction mixture by thin-layer chromatography.

Under analogous conditions, from *tert*-butylacetylene we obtained a brown viscous oil. According to the GC–MS data, it was a complex mixture of products among which we identified di-*tert*-butyldiacetylene. No copper complexes with *tert*-butylacetylene condensation products were detected.

Determination of the structure of diphenyldiacetylene copper complex **II** was hindered because of its very poor solubility in organic solvents; we failed to obtain a single crystal of **II** suitable for X-ray analysis. The IR spectrum of **II** lacked absorption bands typical of a free triple bond (ν 2020–2200 cm^{-1}), but absorption bands assignable to aromatic moieties were present at 1500–1440 cm^{-1}. Furthermore, no ν_{C-H} absorption was observed in the spectrum. Stretching and bending vibrations of the ν_{C-H} bond in phenylacetylene give rise to absorption bands at 3291 cm^{-1} and 656 and 621 cm^{-1}, respectively. The mass spectrum of **II** contained fragment ion peaks with *m/z* 404 (2%), 220 (100%), 102 (20%), 101 (11%), 77 (2%), and 63 (3%). These peaks may be assigned to cations derived from tetraphenyloctatetraene, diphenyldiacetylene, and phenylacetylene and [PhC≡C]$^+$, [Ph]$^+$, and [Cu]$^+$ ions, respectively. Compound **II** is active in the ESR spectrum, whereas initial copper nanoparticles give no ESR signal. The ESR signal of **II** at 295 is a single partially structured line arising from exchange interaction between copper(II) ions.

Complex **II** underwent decomposition by the action of acids, bases, and compounds capable of coordinating metal ions (Scheme 1).

Scheme 1.



For example, compound **II** reacted at room temperature with fluoroalkyl-containing β-diketone **IV** and β-aminovinyl ketone **V** to produce chelates **VI** and **VII**, respectively. By heating complex **II** in boiling dimethylformamide (DMF) we obtained colorless crystals. According to the X-ray diffraction data, these crystals were a new "parquet"-like modification of diphenyldiacetylene (**III**) (Scheme 1, Fig. 1). The

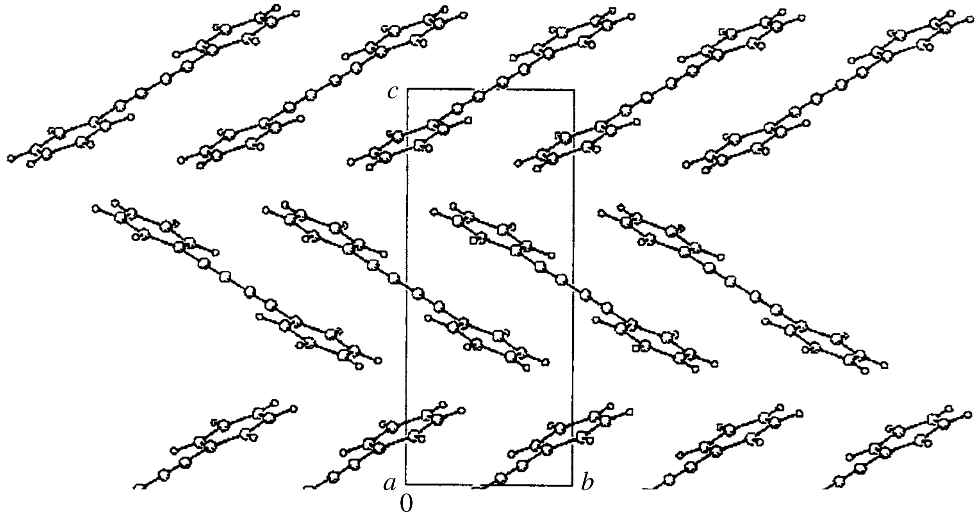


Fig. 1. Packing of diphenyldiacetylene (**III**) molecules in crystal.

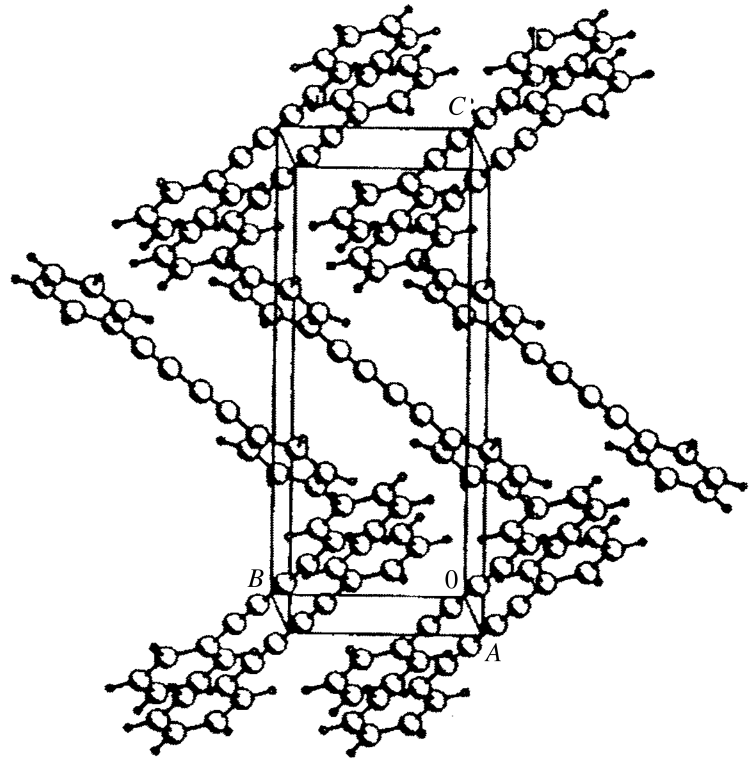


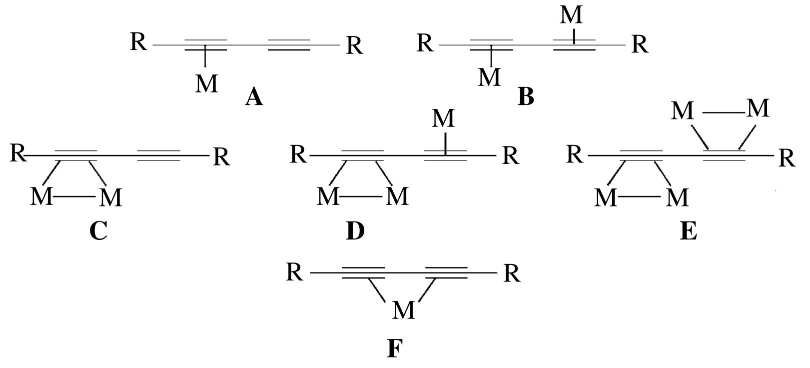
Fig. 2. Packing of diphenyldiacetylene molecules in crystal according to the data of [4].

second product was copper(II) dimethylformamide complex with characteristic parameters of the ESR spectrum.

The Cambridge Crystal Structure Database (CCSD) contains two entries related to the crystal structure of diphenyldiacetylene. Surette et al. [4] isolated compound **III** as yellow crystals by successive treatment of phenylacetylene with butyllithium and copper cyanide. Figure 2 shows crystal packing of diphenyldiacetylene molecules according to the data of [4]. Fronczek and Erickson [5] performed X-ray analysis of a sample of commercial diphenyldiacetylene from Aldrich. The results were in a good agreement with those reported in [4]; the coordinates and equivalent thermal parameters of non-hydrogen atoms in molecule **III** were given, but packing of molecules **III** in crystal was missing. It should be noted that the crystals examined in [5] were colorless needles as in our case.

The chemical behavior of compound **II** in combination with the analytical data and IR, ESR, and mass spectra allowed us to presume that this compound is a complex of diphenyldiacetylene with copper. Several coordination modes are known for diyne metal complexes; among these, monodentate (**A**, **B**) and bridging modes (**C**–**F**) are distinguished [6] (Scheme 2).

Scheme 2.



Modes of coordination of diynes with metals.

There are numerous published data on the structure of complexes of diphenyldiacetylene with different metals: Pt, Nb, Rh, Ru, Ni, Fe. Most of them are characterized by monodentate coordination like **A** [7–11]; rare examples of coordination like **D** [12] and **E** [6] were also reported. However, no data on the crystal structure of phenylacetylene or diphenyldiacetylene copper complexes have been deposited to the CCSD. The elemental composition and spectral parameters of complex **II** correspond to monodentate coordination like **B**.

Our results demonstrate that the use of copper and copper oxide nanopowders in the condensation of acetylene derivatives is fairly promising. Products of such condensations are compounds having conjugated double and triple bonds, which are potential organic semiconductors. It also seems to be reasonable to examine the conductivity of their complexes with transition metals.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) from solutions in CDCl3 using tetramethylsilane as internal reference. The IR spectra were obtained in the range from 4000 to 450 cm^{-1} on a Spectrum One B spectrometer with Fourier transform from samples dispersed in mineral oil. The mass spectra (electron impact, 70 eV) were run on a MAT INCOS50 spectrometer with direct sample admission into the ion source. Gas chromatographic–mass spectrometric analysis was performed on a Varian Saturn 2100T GC–MS system (GC 3900); VF-5ms capillary column, 30 m × 0.25 mm; carrier gas helium, flow rate 1 ml min^{-1}; oven temperature programming from 40°C (3 min) to 200°C at a rate of 20 deg min^{-1}. The ESR spectra were recorded on an ADANI PS 100X spectrometer (Belarus).

Preparation of copper nanopowders. Copper nanopowders were prepared by condensation of copper vapor in argon [2]. Copper oxide nanopowders were prepared in a similar way using argon–oxygen mixtures with different compositions. By varying the gas flow rate and pressure, nanopowders with an average particle size of 10 to 100 nm can be obtained. The phase compositions were determined using a DRON-6 diffractometer. The average particle size was estimated from the diffraction line broadening, as well as from the data of electronic microscopy.

Reaction of phenylacetylene (I) with copper and copper oxide nanopowders. Copper complex II. Phenylacetylene (**I**), 1.02 g, was added to 0.01 g of a nanosize copper powder (dark blue), and the mixture was kept for 5 days at ~20°C. A bright yellow powder-like product (insoluble in organic solvents) was formed. When the reaction was complete (visual control), the yellow crystals were washed in succession with different solvents to remove organic impurities, the product being dried after each washing. The chloroform and benzene washings contained trace amounts of diphenyldiacetylene which was identified by comparing with an authentic sample (TLC); the acetone washings contained no organic substances. Complex **II** had mp 170°C (decomp.). IR spectrum, ν, cm^{-1}: 1594, 1571, 1482, 1440 (C–C_{arom}); 1174, 1155, 1068, 1026 (C–H_{arom}); 744, 682 (ν C–H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 404 (2); 202 (100) [PhC≡C–C≡CPh]$^{+}$; 102 (18); 101 (11) [PhC≡C]$^{+}$; 88 (7); 77 (2) [Ph]$^{+}$; 74 (5); 63 (3). Found, %: C 58.38; H 3.02. *M* 349, 347. $C_{16}H_{10}Cu_2$. Calculated for monodentate coordination of diphenyldiacetylene with copper (**B**), %: C 58.35; H 3.06.

Diphenyldiacetylene (III). Complex **II**, 0.6 g, was heated in 10 ml of boiling DMF until the yellow precipitate disappeared. The solvent was evaporated, and the residue was recrystallized from hexane to isolate colorless crystals of compound **III**. Yield 0.4 g, mp 82–84°C. ^{1}H NMR spectrum, δ, ppm: 7.24–7.38 and 7.5–7.54 (5H, C_6H_5). IR spectrum, ν, cm^{-1}: 2149 (C≡C); 1592, 1569, 1485, 1439 (C–C_{arom}); 1286, 1178, 1157, 1068, 1025 (C–H_{arom}); 755, 686 (δ C–H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): [PhC≡C–C≡CPh]$^{+}$ 202 (100); [PhC≡C]$^{+}$ 101 (11.32); [Ph]$^{+}$ 77 (1.50). Found, %: C 95.02; H 4.98. *M* 202, 255. $C_{16}H_{10}$. Calculated, %: C 95.01; H 4.98.

Copper complex of 4,4,5,5,6,6,7,7-octafluoro-1-phenylhept-2-en-1-one (VI). A mixture of 0.7 g of complex **II** and 4,4,5,5-tetrafluoro-1-phenylbut-2-en-1-one was kept for four weeks at room temperature. The mixture changed its color. It was dissolved in acetone, unreacted complex **II** was filtered off, the filtrate was evaporated, and the residue was reprecipitated from chloroform with hexane. Yield of (4,4,5,-5,6,6,7,7-octafluoro-1-phenylhept-2-en-1-onato)copper(II) (**VI**) 0.4 g, light green powder, mp 202–204°C. IR spectrum, ν, cm^{-1}: 1605 (C=C–C=O); 1598, 1576, 1488, 1461 (C–C_{arom}). Found, %: C 41.18; H 1.68. *M* 757, 915. $C_{26}H_{14}CuF_{16}O_4$. Calculated, %: C 41.20; H 1.86; F 40.11.

Copper complex of 3-amino-1-phenyl-4,4,5,5,6,-6,7,7-octafluorohept-2-en-1-one (VII). A mixture of 1.0 g of 3-amino-4,4,5,5,6,6,7,7-octafluoro-1-phenylhept-2-en-1-one (**V**) and phenylacetylene copper complex **II** in hexane was kept for 7 days. The yellow precipitate turned green, while the solution remained colorless. The solvent was distilled off, the residue was dissolved in acetone, the mixture was filtered, the filtrate was evaporated, and the residue was recrystallized from hexane. Yield of bis(3-amino-4,4,5,5,6,6,-7,7-octafluoro-1-phenylhept-2-en-1-onato)copper(II) (**VII**) 0.78 g (70%), dark green crystals, mp 224–226°C. Found, %: C 41.51; H 2.03; N 3.52; *M* 755, 946. $C_{26}H_{16}CuF_{16}O_2N_2$. Calculated, %: C 41.31; H 2.13; N 3.70.

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REFERENCES

1. Sergeev, G.B., *Usp. Khim.,* 2001, vol. 70, no. 10, p. 915.
2. Gen, M.Ya., *Usp. Khim.,* 1969, no. 12, p. 2249.
3. *Comprehensive Organic Chemistry,* Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 1. Translated under the title *Obshchaya organicheskaya khimiya,* Moscow: Khimiya, 1981, vol. 1, p. 268.
4. Surette, J.K.D., MacDonald, M., Zaworotko, M.J., and Singer, R.D., *J. Chem. Crystallogr.,* 1994, vol. 24, no. 10, p. 715.
5. Fronczek, F.R. and Erickson, M.S., *J. Chem. Crystallorg.,* 1995, vol. 25, no. 11, p. 737.
6. Maekawa, M., Munakata, M., Kuroda-Sowa, T., and Hachiya, K., *Inorg. Chim. Acta,* 1995, vol. 231, p. 213.
7. Ursini, C.V., Dias, G.H., Horner, M., Bortoluzzi, A.J., and Morigaki, M.K., *Polyhedron,* 2000, vol. 19, p. 2261.
8. Garcia-Yerba, C., Carrero, F., Lopez-Mardomingo, C., Fajardo, M., Rodriguez, A., Antinolo, A., Otero, A., Lucas, D., and Murgnier, Y., *Organometallics,* 1999, vol. 18, p. 1287.
9. Wernwe, H., Gevert, O., and Haquette, P., *Organometallics,* 1997, vol. 16, p. 803.
10. Bruce, M.I., Zaitseva, N.N., Scelton, B.W., and White, A.H., *J. Organomet. Chem.,* 1997, vol. 93, p. 536.
11. Yamazaki, S., Deeming, A.J., and Speel, D.M., *Organometallics,* 1998, vol. 17, p. 775.
12. Maekawa, M., Munakata, M., Kuroda-Sowa, T., and Hachiya, K., *Polyhedron,* 1995, vol. 14, p. 2879.