Reaction of thiophosphate 14 with PCl_5. PCl_5 (3.97 g) was cautiously added to a solution of thiophosphate **14** in $CHCl_3$ (20 mL). The mixture was refluxed for 30 min. The volatile compounds were distilled off *in vacuo* (10 Torr) at 70 °C. $CHCl_3$ was added to the residue, and the solution was passed through a porous funnel with SiO_2 to remove resinous admixtures. The solvent was evaporated *in vacuo*, and the residue was distilled to give acid chloride **15**, b.p. 98—110 °C (0.1 Torr), d_4^{20} 1.2261; n_D^{20} 1.5080. Found (%): C, 28.56; H, 5.40; P, 12.09. $C_6H_{14}Cl_2NOPS$. Calculated (%): C, 28.80; H, 5.60; P, 12.40. ^{31}P NMR, δ: +38.

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Received March 4, 1992;
in revised form July 19, 1993

Synthesis of 1-morpholino-1-(phenylethynyl)cycloalkanes from enamines and phenylacetylene in the presence of Cu(I) halides

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1-Morpholino-1-(phenylethynyl)cyclopentane and 1-morpholino-1-(phenylethynyl)cyclohexane were obtained by reactions of enamines, derivatives of cyclic ketones, with phenylacetylene in the presence of CuI. A scheme for catalysis by Cu(I) compounds with the intermediate formation of copper phenylacetylide and iminium salts was suggested.

Key words: 1-amino-1-(phenylethynyl)cycloalkanes; enamines; phenylacetylene, copper(I) halides; copper acetylides; Mannich reaction; iminium salts.

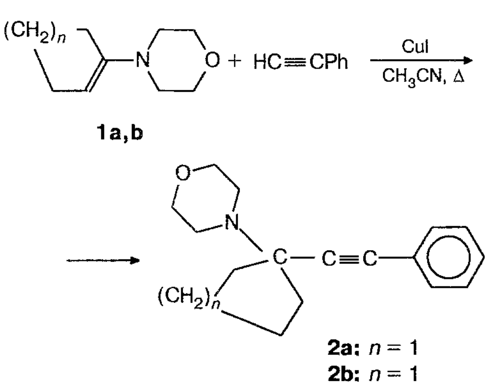
The addition of nonactivated terminal acetylenes to the double bond of enamines, derivatives of butyric and isobutyric aldehydes, catalyzed by Cu(I) compounds has been described previously.[1]

We have found that enamines **1a,b**, the derivatives of cyclic ketones, also readily react with phenylacetylene on heating in acetonitrile in the presence of stoichiometric or catalytic amounts of CuI to give 1-morpholino-1-(phenylethynyl)cycloalkanes **2a,b** (Scheme 1).

It was shown by chromatography that compounds **2** are also formed if CuCl or CuBr are used. In Ref. 1, only the catalytic action of Cu(I) compounds was stated.

It is noted in a review[2] devoted to the Mannich reaction (which can also occur *via* enamines as intermediate compounds) that Cu(I) salts increase the nucleophilicity of acetylene substrates toward Mannich rea-

Scheme 1



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 169—170, January, 1994.

gents. On the other hand, it is well known that terminal acetylenes form acetylides with Cu(I) salts in the presence of nitrogen-containing bases capable of accepting HX.[3] If enamines **1a,b** act as HX acceptors, then copper phenylacetylide and iminium salts (**3a,b**) should jointly appear in the system. As we showed previously,[4] the latter can react in boiling acetonitrile to give products of the aminomethylation of 1-morpholino-1-(phenylethynyl)cycloalkanes **2a,b**, while the CuI regenerated can be involved in the next cycle, *etc.*

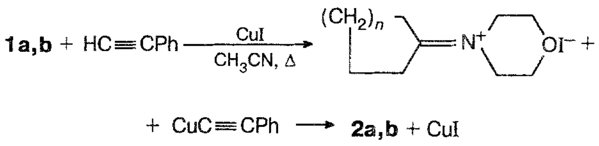
The IR spectra of compounds **2a,b** contain no absorption bands of the triple bond. The structure of these compounds was determined by Raman and ^{1}H and ^{13}C NMR spectral data.

Experimental

^{1}H NMR and ^{13}C NMR spectra were obtained on Tesla BS-487C (80 MHz) and Tesla BS-567 (100 MHz) spectrometers, respectively, using HMDS as the internal standard. Raman spectra were recorded for solid samples on a Ramanor-HG2S instrument; excitation was performed by an Ar^+ laser, 5145 Å.

1-Morpholino-1-(phenylethynyl)cyclopentane (2a). Enamine **1a** (3 mL) (*cf.* Ref. 5) was added with heating to a vigorously stirred suspension of CuI (0.4 g) in acetonitrile (15 mL) and phenylacetylene (2 mL). The mixture was refluxed for 1 h and cooled, then 25 % aqueous ammonia (10 mL) and water (20 mL) were added. The mixture was extracted with chloroform (2×20 mL), the solvent was distilled off, and the residue was recrystallized from hexane to give 4 g (80 %) of colorless crystals of **2a**, m.p. 84—86 °C. Found (%): C, 80.10; H, 8.56; N, 5.43. $C_{17}H_{21}NO$. Calculated (%): C, 80.00; H, 8.23; N, 5.50. ^{1}H NMR (CD_3CN), δ: 7.28 (m, 5 H, Ph); 3.58 (t, 4 H, CH_2O); 2.55 (t, 4 H, CH_2N); 1.70 (m, 8 H, CH_2). Signals of acetylenic carbon atoms in the ^{13}C NMR spectrum ($CDCl_3$), δ: 90.68 (CPh), 85.91 (${>}\mathrm{C}-\mathrm{C}$). The Raman spectrum contains a doublet of lines ν(C≡C) 2209 and 2217 cm^{-1}.

Scheme 2



1-Morpholino-1-(phenylethynyl)cyclohexane (2b). Enamine **1b** (*cf.* Ref. 5) (3.5 g), phenylacetylene (2.2 mL), and CuI (4 g) in acetonitrile (20 mL) were refluxed for 30 min and cooled, then 25 % aqueous ammonia (10 mL) and water (20 mL) were added. The mixture was extracted several times with hot hexane and then with chloroform. The solvents were distilled off, and the residue was recrystallized from hexane to give 3.3 g (59 %) of colorless crystals of compound **2b**, m.p. 100—102 °C. Found (%): C, 80.23; H, 8.69; N, 5.61. $C_{18}H_{23}NO$. Calculated (%): C, 80.30; H, 8.55; N, 5.20. ^{1}H NMR (CD_3CN), δ: 7.25 (m, 5 H, Ph); 3.55 (t, 4 H, CH_2O); 2.50 (t, 4 H, CH_2N); 1.82—1.45 (m, 10 H, CH_2). Signals of acetylenic carbon atoms in the ^{13}C NMR spectrum ($CDCl_3$), δ: 89.90 (CPh), 86.31 (${>}\mathrm{C}-\mathrm{C}$). The Raman spectrum contains a doublet of lines ν(C≡C) 2211 and 2215 cm^{-1}.

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Received October 14, 1993