REACTIONS OF COPPER AND SILVER ACETYLIDES WITH HYDRAZONE BROMIDES — A NEW ROUTE TO 1,3,5-SUBSTITUTED PYRAZOLES

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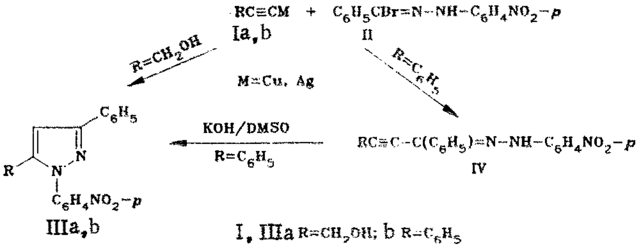
We have found that substituted copper and silver acetylides (I) readily ethynylate hydrazone bromides in refluxing acetonitrile.

For N-benzylidene-N'-p-nitrophenylhydrazone bromide (II) it has been shown that the reaction product depends on the acetylenyl R substituent and can have both a cyclic (pyrazoles III) and a linear (acetylenyl ketone hydrazone, IV) structure:



I, IIIa R=CH_2OH; b R=C_6H_5

Hydrazone IV may subsequently be quantitatively converted to pyrazole IIIb [1] by treatment with KOH in DMSO at 60-80°C for several minutes.

A solution of the hydrazone bromide II (4 mmole) [2] and copper phenylacetylide (R = C_6H_6, 6 mmole) [3] in acetonitrile (20 ml) was refluxed for 0.5 h. The reaction mixture was filtered hot and the filtrate cooled to give IV in 36% yield with mp 179-183°C (from octane) and M^+ 341. Use of the copper acetylide of propargyl alcohol (R = CH_2OH) [3] under analogous conditions (1 h reflux) gave 1(p-nitrophenyl)-3-phenyl-5-hydroxymethylpyrazole (IIIa) in a 33% yield with mp 132-137°C and M^+ 295.

The IR spectrum of hydrazone IV showed absorption bands at 2185 (C≡C) and 3285 (N–H) cm^{-1} which were absent in the spectra of the pyrazoles III. Elemental analytical data for all compounds was in agreement with that calculated.

LITERATURE CITED

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