LETTERS TO THE EDITOR

CATALYST FOR ACETYLENIC CONDENSATION

M. S. Shvartsberg, A. A. Moroz,
and I. L. Kotlyarevskii

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It was found that the rate of the catalytic method for the direct insertion of acetylenic substituents into an aromatic ring [1] is greatly increased if instead of metallic Cu, a Cu(I) salt is used as the catalyst in the presence of K_2CO_3

$$\mathrm{ArI} \xrightarrow{\mathrm{HC{\equiv}CR}} \mathrm{ArC \equiv CR}$$

In this connection weaker bases (amines, KF, etc.) are ineffective. The proposed method is essentially a catalytic method and, in contrast to [2], does not require the use of dry copper acetylides. At the same time, the condensation rate in this case is dependent on the amount of CuX. For example, the time required for the condensation of methyl o-iodobenzoate with $C_6H_5 \equiv CH$ in the presence of CuI, under conditions analogous to those given in [1], was (the amounts of CuI are given in moles per mole of ArI, while the time is given in hours): 3,45 min; 2,1.5; 1.5,2; 0.5,3.5; 0.07,8.5. The yield of o-carbomethoxytolan was 80%. For comparison: with Cu as the catalyst [1] the reaction is completed in 17 h, while with copper phenylacetylide it is completed in 4.5 min.

The advantages of the method made it possible to synthesize arylacetylenic alcohols without resorting to protection of the hydroxyl group. Thus, 1-(o-carbomethoxyphenyl)-3-methyl-1-butyn-3-ol was obtained in 90% yield; with 3 moles of $HC \equiv CC(CH_3)_2OH$ and 1.5 moles of CuI the reaction was ended in less than 3 h.

LITERATURE CITED

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Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR. Novosibirsk State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, p. 981, April, 1972. Original article submitted December 23, 1971.