

A NOVEL MERCURIC ION CATALYSED REACTION OF
1,6-DIARYLOXY-2,4-HEXADIYNES TO 4,4'-BICHROMENES

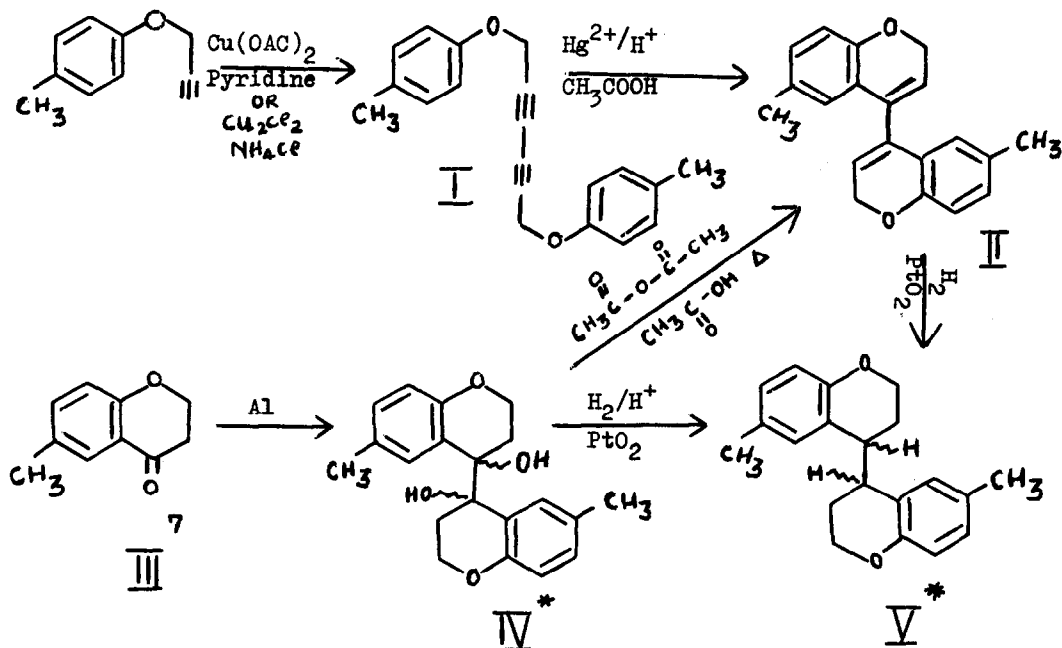
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(Received in UK 25 October 1973; accepted for publication 2 November 1973)

One of the classic reactions in the chemistry of acetylenes is the hydration of $\text{C}\equiv\text{C}$ bond, catalysed by mercuric salts and by other reagents¹. While this reaction has been investigated in detail in many acetylenic systems^{2,3}, so far no detailed study on the hydration of various functionally substituted conjugated diynes has appeared, though the literature records a few reports on the hydration of conjugated-diynes, diynediols and diyneones⁴. In connection with our work in this area we were interested in studying the hydration of symmetrical and dissymmetrical 1,6-diaryloxy-2,4-hexadiynes. The formation of 4-aryloxymethylchromenes in an attempted hydration of 1,4-diaryloxy-2-butyne^{5,6} further motivated us to take up this study. In this communication we report a facile and novel mercuric ion catalysed reaction of 1,6-di-(p-methylphenoxy)-2,4-hexadiyne(I) to 6,6'-dimethyl-4,4' bichromene(II), a new class of bichromenes, hitherto unknown in literature.

Glaser oxidative coupling of p-methylphenyl propargyl ether afforded 1,6-di-(p-methylphenoxy)-2,4-hexadiyne(I)[®] (82%), m.p. 107°. There was no reaction when the diynylbisether I was refluxed with mercuric acetate or mercuric sulphate in alcohol or aqueous dioxane, but when an acetic acid solution of it was stirred at room temperature with catalytic amounts of red mercuric oxide and a few drops of conc. sulphuric acid, a pale brown solid (61%), m.p. 110-115° was obtained. Purified by column chromatography over alumina (hexane elution), it melted at 115-16° and was found to be isomeric with the starting material as indicated by its elemental analyses and mass spectrum. On the basis of its analytical and spectral data, it has been identified as 6,6'-dimethyl-4,4'-bichromene(II), a new class of bichromenes, not described in literature so far.

The structure of the bichromene II was confirmed by an independent synthesis outlined below:



Acknowledgement: We are thankful to CIBA Research Centre, Bombay for some of the analytical and spectral data. Our thanks are due to Prof. C.A. Grob for a generous gift of propargyl alcohol and interesting discussions. One of us (RN) thanks the CSIR for the award of a Junior Research Fellowship.

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ⓈAnalytical and spectral data were fully consistent with the structures of all new compounds reported in this paper.

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+Part of this work was taken from the M.Sc. Dissertation (1972) of K. Virupaksha Reddy.

*The crude diol, which is probably a mixture of the dl and meso isomers, was used as such for the dehydration and hydrogenolysis reactions. The stereochemistry of the solid diol, m. p 195° and of the 4,4'-bichromene, m.p. 142° have not been established.