

Reaction of Acetophenone with Cupric Bromide

SAYED M. IFZAL*, RUKHSANA AKHTAR, ARIF KAZMI AND MAZHER KHAN

Department of Chemistry, University of Karachi, Karachi, Pakistan.

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Introduction

In recent years cupric halides under various reaction conditions have been employed for halogenations of a variety of compounds. Cupric bromide in dioxan¹ or ethyl acetate - chloroform² has been reported to be a selective reagent for brominating the side chain of aryl methyl ketones. Jemison³ has, however, reported instances in which unclear bromination of several aryl methyl ketones predominates over the side chain bromination. More recently Marmor⁴ has used cupric bromide in 1,2 - dimethoxyethane (DME) for monobromination of the intermediate (I) to (II) in an improved synthesis of 5-alkylresorcinols.

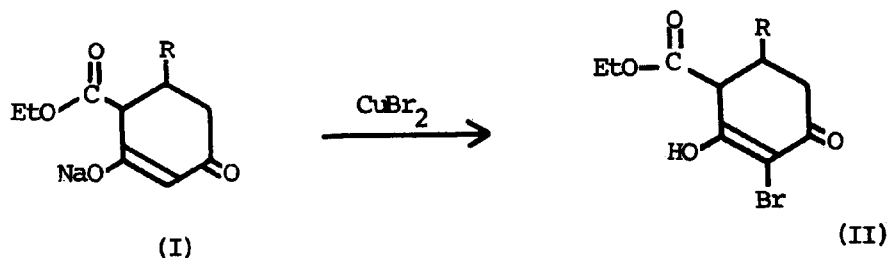
In the reaction of 1- and 2-alkoxynaphthalenes with either cupric chloride or cupric bromide it has been observed⁵ that 2-alkoxynaphthalenes are halogenated in high yield at the 1-position while the 1-alkoxynaphthalenes are converted into 1-alkoxy-4-halogenonaphthalenes and 4,4'-dialkoxy-1,1'-binaphthyls. Similarly monohalogenation at the alpha position of acetone⁶ and propiophenone⁷ have also been reported in the reactions with cupric chloride.

We wish to report here the formation of a condensation product viz. 1,3,5 - triphenylbenzene (IV) obtained on heating a large excess of acetophenone (III) with cupric bromide. Two other products in low yield were also obtained whose structural investigations are under way.

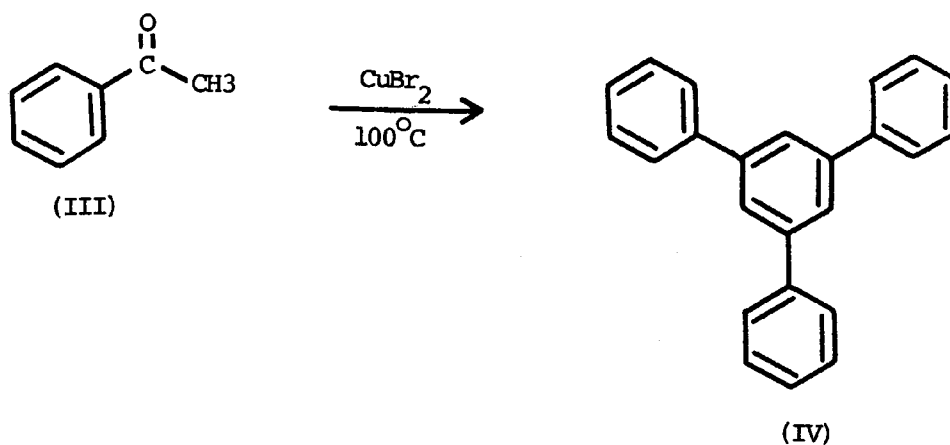
It has also been observed by us that cupric iodide fails to react with acetophenone under identical conditions, while the reaction is accelerated on using cupric chloride instead of bromide. If, however, equimolar quantities of the reactant are taken using solvents like benzene or dimethylformamide the yield of 1,3,5-triphenylbenzene is reduced to almost negligible amount and a mixture of several products results which is difficult to separate. We are presently engaged in the detailed studies of the reactions of cupric halides with various types of organic compounds the results of which will be communicated later.

Experimental

To acetophenone, 100ml (0.8 moles), was added cupric bromide, 10g (0.05 moles), and the mixture stirred at 100°C for four hours. The reaction mixture was cooled, allowed to stand overnight and filtered. The filtrate 'A' was set aside, while the residue consisting of a mixture of dark brown and light yellow crystalline material was washed thrice with methanol. The washing removed the dark brown material giving crude yellow crystalline powder (5.5g) m.p. 174 - 178°C. This on recrystallisation from chloroform-ethanol (1:1) gave light yellow needles and was identified as 1,3,5-triphenylbenzene m.p. 178 - 179°C (lit. 176°C); IR (KBr) ν_{\max} 3030 & 3015 due to =C-H str; 1595, 1495 & 1410 in plane



*To whom all correspondence may be addressed.



C=C str; 1080 & 1030 in plane and 860 & 695 cm^{-1} due to out of plane C-H deformations; UV: $\lambda_{\text{max}}^{\text{EtOH}}$ at 253 ($\epsilon = 56,580$); NMR (CCl_4) δ 7.35, 7.45 and 7.62 due to 3,6 & 9 protons respectively; mass m/e: 306 (100% - M^+), 229, 153, 152, 77 and 75.

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