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NOTE

Synthesis of Dimer by Using Copper Metal with and without Solvent

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2(4′-Chlorophenyl)-3-iodo-6-chloro-8-bromo flavone condensed with copper powder as well as with copper powder in presence of DMF medium gives 2(4′-chlorophenyl)-6-chloro-8-bromo diflavone. The structure of these dimers were confirmed by spectral data and chemical analysis.

The coupling of aryl halides in presence of copper is the Ullman reaction. This reaction is of broad scope and has been used to prepare many symetrical and unsymmetrical biaryls[1]. When a mixture of two different aryl halides is used three different products are possible but often only one is obtained, *e.g.*, picryl chloride and iodobenzene gave only 2,4,6-trinitrobiphenyl[2].

In aryl halide reactivity of halide group is I > Br > Cl[3]. The electronegative group in another position activates aromatic compounds in this type of coupling reactions. The reactivity of NO_2 group in coupling reactions is *ortho* > *para* > *meta*[4]. 2-Iodo-nitrobenzene is very reactive but 3-iodo and 4-iodo derivatives are about as reactive as iodobenzene[3]. Even functionalised aryls such as ferrocene can be coupled using copper salt[5]. The best yield is observed when one aryl halide is very reactive and another is relatively less reactive.

The use of bromides and chlorides maximises unsymmetrical coupling while iodo compounds generally give symmetrical coupling product[6].

Alkynes can be coupled with a variety of compounds[7], including reactions that involve alkynyl copper derivatives.

In Glaser reaction[8], phenyl propyne reacts with basic copper chloride to give diyne in 90% yield. In Gadiod Chodkiewich coupling[9], bromoalkyne reacts with monoalkyne in presence of $CuCl_2$ and an amine to give diynes.

In this communication we are reporting the formation of diflavone in presence of copper in DMF solvent and without DMF solvent.

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Preparation of 2(4′-chlorophenyl)-6-chloro-8-bromo diflavone (without solvent), Ia

2(4′-Chlorophenyl)-3-iodo-6-chloro-8-bromo flavone (0.02 mole) and copper powder (0.02 mole) were taken in a hard glass tube. The tube was sealed with rubber cork and plaster of Paris. The mixture was heated on oil bath for 1 h, maintaining the temperature between 200–250°C. The hard mass was extracted with hot ethanol, crystallised from alcohol to give 2(4′-chlorophenyl)-6-chloro-8-bromo diflavone, 233°C, yield 75%.

OR

Preparation of 2(4′-chlorophenyl)-6-chloro-8-bromo diflavone (with solvent), Ia

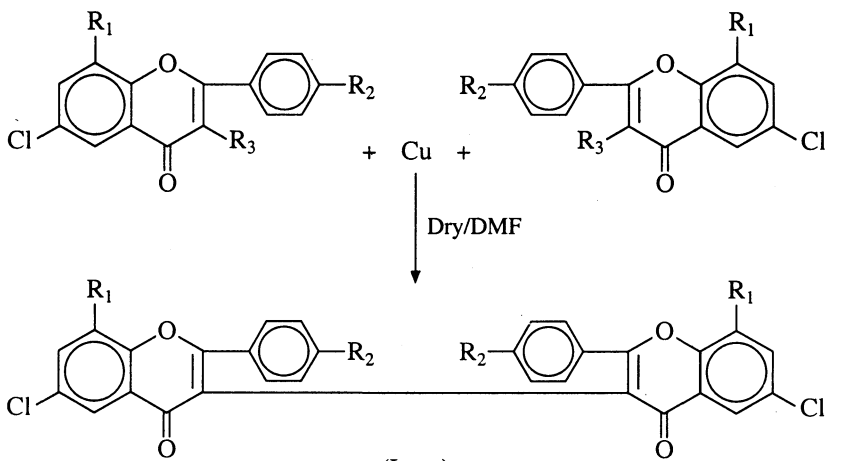
2(4′-Chlorophenyl)-3-iodo-6-chloro-8-bromo flavone (0.02 mole) was taken along with copper powder (0.02 mole). 20 mL of DMF was poured in it. The mixture was refluxed for 1.5 h. The reaction mixture was cooled, diluted with water, the crude mass was crystallised from ethanol to give 2(4′-chlorophenyl)-6-chloro-8-bromo diflavone (**Ia**), m.p. 233°C, yield 75%.

Properties of compound Ia

1. It is mid buff coloured crystalline compound, m.p. 233°C, yield 75%.
2. From analytical data molecular formula was found to be $C_{30}H_{12}O_4Cl_4Br_2$, the molecular weight being found to be 738.0.
3. The IR spectrum was recorded in nujol.

1652.00	ν(—C=O, stretching),
1611.10, 1594.90, 1455,60	ν(—C=C—, in aromatic ring),
1286.10	ν(Ar—O, stretching),
762.00	ν(—C—Cl, stretching) and
642.60 cm^{-1}	ν(—C—Br, stretching)

4. The PMR was recorded in $CDCl_3$ with TMS as an internal standard 6.80–8.30 δ (m, 12H, Ar—H).



(Ia–n)

TABLE-1
SYNTHESIS, m.p. (S), YIELD AND COLOUR OF COMPOUNDS

S. No.	R_1	R_2	R_3	m.p. (°C)	yield (%)	Colour
Ia	Br	Cl	I	233	75	Mid buff
Ib	Br	Cl	Br	233	75	Mid buff
Ic	Br	NO_2	I	276	70	Leaf brown
Id	Br	NO_2	Br	276	70	Leaf brown
Ie	NO_2	Cl	I	259	73	Mid buff
If	NO_2	Cl	Br	259	73	Mid buff
Ig	NO_2	NO_2	I	307	75	Mid buff
Ih	NO_2	NO_2	Br	307	75	Leaf brown
Ii	H	Cl	I	212	78	Mid buff
Ij	H	Cl	Br	212	78	Pale cream
Ik	H	NO_2	I	268	80	Golden brown
Il	H	NO_2	Br	268	80	Golden brown
Im	H	NH_2	I	278	75	Dark brown
In	H	NH_2	Br	278	75	Dark brown

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