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Synthesis of new azo dyes via Suzuki coupling

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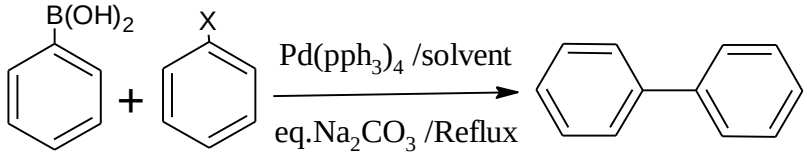
Abstract

The synthesis of new azo dyes have been achieved by coupling reaction of pyrimidine derivative with different phenolic compounds , the products have been treated with 2- fluoro boronic acid by Suzuki coupling reaction to give new azo dyes . These compounds have been characterized by spectroscopic methods (FTIR , UV-VIS) ,TLC and melting point .

Keyword : azo dyes , Suzuki coupling , pyrimidine derivative

Introduction

The Suzuki coupling is one of the most common cross-coupling methods in modern organic synthesis[(1)]because this reaction is due in particular to widespread industrial use for the production of complex specially chemicals , such as building blocks for active pharmaceutical ingredients , electronic materials or high performance metallocene catalysts[(2)]. In Suzuki coupling biaryl compounds can be produced by coupling boronic acid with aryl halide[(3)] (Figure 1) .



(Figure 1): Suzuki coupling

The importance of azo dyes in Synthesis has increased over the past few decades[(4)] Because azo compounds are highly colored , and they constitute an important part of the dye industry[(5)].

Experimental

The melting points were measured on staurat (M.P./SMP) apparatus (Melting points are uncorrected) .The FTIR spectra were recorded on shimadzu FTIR -8400S spectrophotometer using KBr disc . The UV-VIS. Spectra were recorded on shimadzu UV-VIS.(1600 spectrophotometer) . Analytical silica gel TLC plates 60 F254 were purchased from Merck. All reagents were obtained from commercial suppliers and were used without further purification.

General Procedure :

Synthesis of Azo compounds(B2-7) via coupling reaction.

A solution of pyrimidine derivative (431 mg ,0.01 m.mole) in 50 ml of HCl (conc.) and a solution of NaNO2 (69 mg , 0.01 m.mole) in 10 ml H2O were added simultaneously with vigorous stirring at **(0-5)C°** and after 10 min. at **(0-5) C°** was rapidly added to solution consist of (0.01 m.mole) of phenolic compound in 25 ml of NaOH (10%) . The reaction mixture was stirred at **(0-5) C°** for 15 min. The solid product obtained was filtered off and washed with water ,and then recrystallized from ethanol (99.9%) .(Scheme 1) .

General Procedure:

Coupling reactions of boronic acid with phenolic compounds **(B2-7)** via Suzuki coupling (Synthesis of comp**.(D9-14) .**

In two-necked round bottom flask under an atmosphere of nitrogen gas was placed correct amount of catalyst (0.02 mg) $(Ph_3P)_4Pd$ with stock solution (made up by mixing (0.01 m.mole) phenolic compounds(**B2-7**) ,(140 mg ,0.001 m. mole) fluoro boronic acid , 5 ml Na_2CO_3(2N) and 15 ml n-propanol) . The mixture was heated vigorously under reflux (water condenser) for 6 hour using heating mantle and maintaining rapid stirring. The reaction progress can be monitored by TLC(n-Hexane- Ethyl acetate 2:1) . After the reaction was completed , the mixture was allowed to cool slowly to R.T. and then cool in ice-bath . The solid product obtained was filtered off and recrystallized from diethyl ether to give coloured compounds **(D9-14) .(Scheme 1) .**

1)) 6- Diphenylamino-5-(2'-fluoro-biphenyl-4-yl azo)-4-(4-hydroxy-naphthalen-1-yl azo)-1-methyl-1*H*-primidin-2-one . **(D9)** .
Yield :.(0.50 g , 77%) , M.P. = 247-246 C° , R_f = 0.50 .

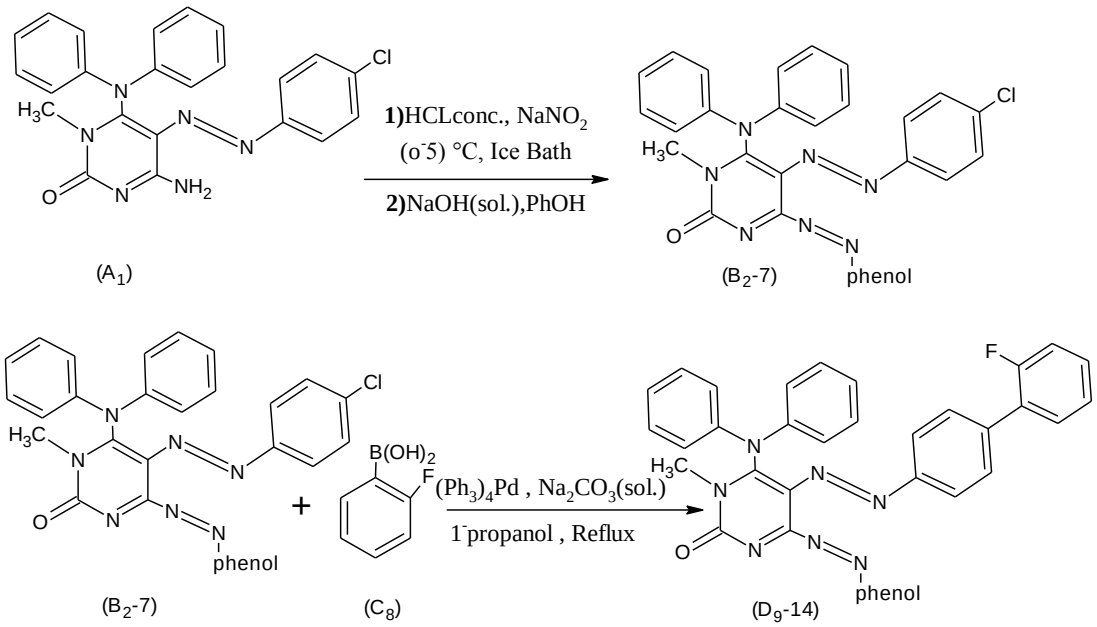
2)) 6- Diphenylamino-5-(2'-fluoro-biphenyl-4-yl azo)-4-(2-hydroxy-naphthalen-1-yl azo)-1-methyl-1*H*-primidin-2-one . **(D10)** .
Yield :.(0.55 g , 85%) , M.P. = 261-260 C° , R_f = 0.48 .

3)) 6- Diphenylamino-5-(2'-fluoro-biphenyl-4-yl azo)-4-(2,5- dihydroxy- phenyl azo)-1-methyl-1*H*-primidin-2-one . **(D11)** .
Yield :.(0.60 g , 88%) , M.P. = 222-221 C° , R_f = 0.65 .

4)) 6- Diphenylamino-5-(2'-fluoro-biphenyl-4-yl azo)-4-(2,4 - dihydroxy- phenyl azo)-1-methyl-1*H*-primidin-2-one . **(D12)** .
Yield :.(0.56 g , 82%) , M.P. = 210-209 C° , R_f = 0.60 .

5)) 6- Diphenylamino-5-(2'-fluoro-biphenyl-4-yl azo)-4-(4 - hydroxy- phenyl azo)-1-methyl-1*H*-primidin-2-one . **(D13)** .
Yield :.(0.50 g , 75%) , M.P. = 197-196 C° , R_f = 0.68.

6)) 5-[6-Diphenylamino-5-(2'-fluoro-biphenyl-4-yl azo)- 1-methyl-2-oxo-1,2-dihydro-primidin-4-yl azo]-2-hydroxy-bezoic acid . **(D14)** .
Yield :.(0.50 g , 78%) , M.P. = 239-238 C° , R_f = 0.54.



Phenol = ((1-Naphthol ,2-Naphthol , Quinol ,Resorcinol , Phenol , Salicylic acid))

Scheme (1) : Synthesized compounds

Results & Discussion

The aim of this work is to synthesize new azo dyes containing poly aromatic rings and two groups azo via Suzuki coupling reaction . The mechanism for the Suzuki coupling involves five steps: 1) Oxidizing addition ; 2) Ligand substitution(Transmetallation) ; 3)Reductive elimination . The palladium(0) species is generated under the reaction conditions from $(Ph_3P)_4Pd$. The boronic acid reduces the Pd(II) to Pd(0) . The palladium(0) complex then oxidatively adds the aryl halide(Pyrimidine derivative) . The halide is then substituted by 2-fluoro boronic acid to give a palladium di aryl complex . Reductive elimination from this complex occurs to give the new organic product and regenerate the Pd(0) catalyst . In Suzuki coupling oxidative addition is often the slowest step (Rate Determining Step)[#].The Suzuki reaction in organic synthesis are that it is very versatile,tolerates numerous functional groups and usually works under gentle conditions and the boronic acids are insensitive to water and oxygen . Synthesis of starting materials ((5-(4-chloro-phenyl azo)-6-diphenylamino-1-methyl-4-phenol azo- 1*H*- pyrimidin- 2-one)) which based on the coupling reaction between diazonium salt of pyrimidine derivative with phenolic compounds in sodium hydroxide solution (B2-7) .Their structures were confirmed by FTIR spectra which show υ(cm^{-1}) 3062(arom.CH) , 3448 (OH group) , 1655 (C=O) , for 1620 (N=N) . Finally treatment of ((5-(4-chloro-phenyl azo)-6-diphenylamino-1-methyl-4-phenol azo- 1*H*- pyrimidin- 2-one)) compounds **(B2-7)** with 2-fluoro boronic acid **(C8)** via Suzuki coupling reaction gives new azo dyes **(D9-14)** , the structures were determined by (FTIR , UV-VIS) spectra[(15)]. Physical and spectral data were listed in table (1 and 2) .

Table (1) Physical data of prepared compounds

NO.	Phenol	Mol.Stru.	M.Wt (g/mol)	M.P.(C°)	Colour
D9	1- Naphthol	$C_{39}H_{28}N_7O_2F$	645.68	247-246	L*.Yellow
D10	2- Naphthol	$C_{39}H_{28}N_7O_2F$	645.68	261-260	Orange
D11	Quinol	$C_{35}H_{26}N_7O_3F$	611.63	222-221	Brown
D12	Resorcinol	$C_{35}H_{26}N_7O_3F$	611.63	210-209	D*.Yello
D13	Phenol	$C_{35}H_{26}N_7O_2F$	595.63	195-194	Yellow
D14	Salicylic acid	$C_{38}H_{26}N_7O_4F$	639.62	239-238	L.Brown

*L= Light , D = Dark.

Table (2) Spectral data of prepared compounds

Comp. NO.	$\lambda_{max.}$ EtOH	FTIR ύ cm^{-1} (KBr disk)				
		C=O	N=N	OH	C-F	C=C
D9	**365**	**1630**	**1597**	**3350**	**1028**	**1543**
D10	**368**	**1635**	**1592**	**3400**	**1026**	**1535**
D11	**295**	**1636**	**1589**	**3300**	**1015**	**1530**
D12	**276**	**1650**	**1597**	**3320**	**1033**	**1540**
D13	**306**	**1636**	**1605**	**3400**	**1035**	**1558**
D14	**320**	**1666**	**1612**	**3518**	**1034**	**1528**

References

1. **L**un X. Yin , (**2007**) , "C-C coupling reactions catalyzed by Heterogenous palladium catalysts" ,**Chem.Rev**., 107 (1) , 133-173 .
2. Norio Miyauria, Akira Suzuki , (**1995**), "Palladium-Catalyzed cross coupling reactions of organoboron compounds " , **Chem.Rev**. ,95(7) , 2457-2483 .
3. Akira Suzuki , (**1998**) , "Recent advances in the cross- coupling reactions of organoboron derivatives with organic electrophils ", **Journal of Organometallic Chemistry** , 576(1999) , 147-168 .
4. S.P. Stanforth , (**1998**) , "Catalytic cross-coupling reactions in biaryl synthesis ", **Tetrahedron** , 54 , 263 .
5. A. Suzuki , (**1991**) , "Synthetic studies via the cross- coupling reaction of organoboron derivatives with organic halides ", **Pure Appl. Chem.** , 63 , 419.
6. S.R.Chemler , D. Trauner , S. J. Danishefsky ,(**2001**) , " The B-alkyl Suzuki-Miyaura cross-coupling reaction :development , mechanistic study and applications in natural product synthesis " **Angew.Chem.Int.Ed.** , 40 , 4545 .
7. Roland Zenk , Steffen Partzsch , (**2003**) , "Organic boronic acids and boronic acid esters in industrial synthesis " ,**Chimica Oggi** ,87, 70-73 .

8. A.R.Martin , Y. Yang ,(**1993**), "Palladium-catalyzed cross-coupling reactions of organoboronic acids" , **Acta Chem. Scand.** , 47,221 .
9. Hyo-Jun Lee , Chang-Woo Cho , (**2011**) , "Chemoselective Suzuki cross-coupling reactions of chiral pyrrolizines" **Bull.Korean Chem.Soc**.,32(1), 359-362 .
10. Robert Franzen , (**2000**), "The Suzuki,the Heck and the Still reaction- three versatile methods for the introduction of new C-C bonds on solid support", **Can.J.Chem.** , 78, 957-962 .
11. R. M. Silverstein ,(**1991**) , "Spectrometric identification of organic compounds",5th ed. ,**John Wiley& Sons**., New York .
12. Furniss S. Brian , (**198**9), "Vogel□s textbook of practical organic chemistry ", 5th ed., **John Wily & Sons.Inc.**, New York .
13. Christopher S. Callam and Todd L. Lowery, (**2001**), "Suzuki cross-coupling reactions: Synthesis of unsymmetrical biaryls in the organic lab.",**Journal of Chemical Edu.** , 78(7) , 947-948 .
14. G.W.Kabalka, Z.Wu &Y.Ju. ,(**2003**) , "Use of organoboron halids in organic synthesis", **Pure Appl.Chem**., 75(9), 1231-1237 .
15. Ibrahim M. El-deeb, Jae C.Ryu & So H. Lee, (**2008**), "Synthesis of new N-aryl pyrimidin-2-amine derivatives using a palladium catalyst",**J.Molecule**s, 13, 818-830.
16. Robert B. Grossman , (**2002**), "The Art of writing Reasonable Organic Reaction Mechanism",2ed ed. , **Springer** , Kentucky University .
17. Jwanro Hassan, Marc Serignon & el.al. , (**2002**), "Aryl-Aryl bond formation one century after the discovery of the Ullmann reaction ",**Chem.Rev**.102, 1359-1469 , Pair -sud university .

تحضير أصباغ ازو جديدة عن طريق أزدواج سوزوكي

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الخلاصة

تم تحضير اصباغ ازو جديدة بالاستفادة من تفاعل الازدواج لمشتق البريميدين مع مركبات فينولية مختلفة ، وتم معاملة النواتج مع 2- فلورو حامض البورونيك عن طريق تفاعل ازدواج سوزوكي حيث تم الحصول على اصباغ ازو جديدة . تم تشخيص المركبات الناتجة بالطرق الطيفية (الاشعة تحت الحمراء ، الاشعة فوق البنفسجية والمرئية) ، كروموتوغرافيا الطبقة الرقيقة ، درجات الانصهار .

الكلمات المفتاحية : اصباغ ازو ، ازدواج سوزوكي ، مشتق البريميدين .