ISOFLAVONES AND ISOFLAVANONES WITH LIGAND COUPLING ROUTE

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Abstract

Arylation of 3-phenylsulphonylchroman-4-ones using Ph_3NCO_3 leading to the synthesis of isoflavones and isoflavones reported.

(Keywords : Arylation, isoflavonenes adn isoflavones)

Introduction

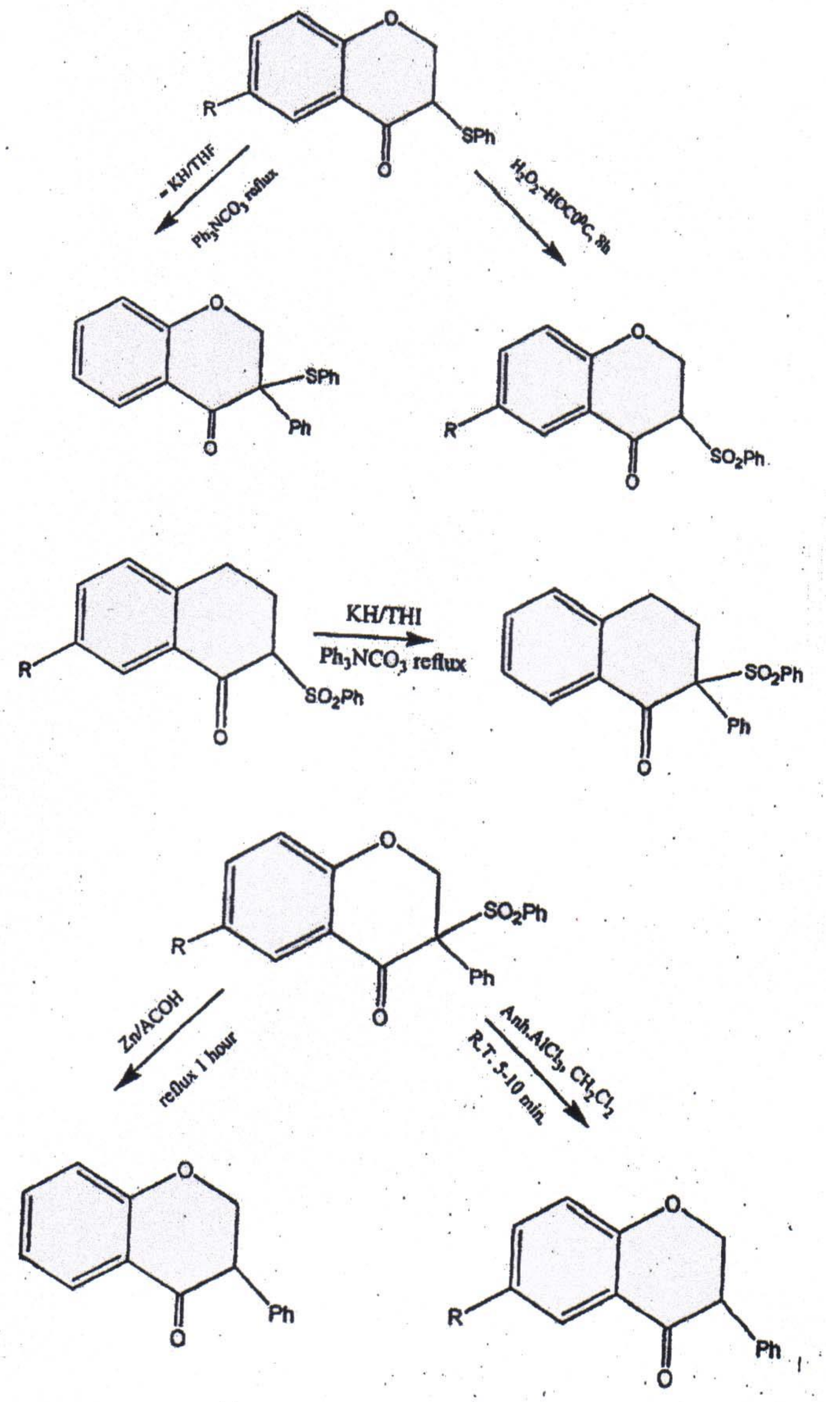
The isoflavanones and other isoflavonoids are important class of biologically active natural products. The biological activities of these compounds include esterogenic, insecticidal, pesticidal and antifungal properties.[2] Even though a nunber of synthetic methods have been described for both isoflavanones[3] and isoflavones[4] except for the palladium catalysed Heck-arylation[5] of chrom 3-en-4-ol acetate, the routes are mainly based on direct ring synthesis.

The recently developed nitrogen (v) regents[6] serve as good arylating reagents for ketones, enols and enolates. The use of these reagents for the synthesis of isoflavanones has been resently reported by Barton et al[7]. However, the method suffers from the disadvantages that the phenylation of chroman-4-one afforded the isoflavanone only in low yield and the reaction could not be stopped at monophenylation stage, whereas phenylation of 3-formylchroman-4-one furnished the diphenylate product following in situdeformylation of monophenlated intermediate. Moreover, owing to the ubiquitous aldol condensation in the presence of a base, 3-formylchloran-4-one leads the formation of the minor amount of dimerised product. Also, the method is not amenable for a direct synthesis of isoflavones.

Experimental

The 3-phenylsulphonylchroman-4-one 3(1mmol) was added to dry THF (7ml) containing potassium hydride (ca.1.2mmol). To this orange enolate solution was added Ph, $BiCO_3$ (1.3 mmol). The mixture was refluxed for 3 h and filtered through celite. The filtrate was oncentrated and purified by column chromatography on silica (hexane-ethyl acetate, 9:1) to furnish the product 4.

All the new compounds reported in this commuication were thoroughly characterised by spectral and analytical data.



Results and Discussion

We now report a simple and high yielding, modified, ligand coupling[8] route for the a-phenylation of chroman-4-ones, which permits the synthesis of both isoflavanones and isoflavones from common intermediates, 3-phenyl-3-sulphonyl chroman-4-ones, in good yield.

3- phenylthiochroman-4-ones la-d were prepared by our recently reported procedure.[9] Compound la was subjected to phenylation using Ph_3BiCO_3 in the presence of KH in tetrahydrofuran (THF). However, the required product 2a was obtained in very low yield (20%). Attempted oxidation of la using various reagent, e.g. $NalO_4$, m-chloroperbenzoic acid (MCPBA) and magnesium monoperoxyphthalate, faiued to yield the desired sulpoxide owing to the occurrence of facile elimination duringn work leading to the chromone. Hence compounds la-d was achieved by refluxing in Zn-HOAc[9-10] for 1 h affording the required isoflavones 5a-d in 80-85% yield (Scheme 3)

Table - 1

Converslon of compound 3 into 4 (scheme-2)

Compound	R	Yield(%)	M.P. t/^{0}C
4a	H	80	205
4b	Me	88	198
4c	Cl	79	226
4d	OMe	85	202

Table - 2

Converslon of compound 4 into 5 and 6 (scheme-3

Compound	R	Yield (%)	M.P. t/^{0}C	Compd.	Yield	M.P. t/^{o}C
5a	H	80	79	6a	95	128
5b	Me	82	50	6b	98	110
5c	Cl	80	110	6c	92	176
5d	OMe	84	108	6d	95	170

All the literature methods tried to order to bring about the elimination of phenylsulfinic acid from compound 4a to obtain the isoflavone were in vain. Surprisingly, treatement of 4a-d with anhydrous $AICI_3$ (1.3 eqiv) in dichloromethane at room temperature for 5-10 min yielded the desired isoflavones 6a-d in almost quantative yield (table-2)

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