

Reaction of Diarylnitrilimines with 3-Arylidene-4-Isothiochromanones. A General Approach to the First Thiadiazaphenanthrene.

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Summary :

A general synthesis of derivatives of 1,2,4-triphenyl-4,10-dihydro-10-thia-3,4-diazaphenanthrene (a new heterocyclic skeleton) in two steps from 3-arylidene-4-isothiochromanones via cycloaddition route is recorded.

As a part of our search about the regiochemistry of the cycloaddition of diarylnitrilimines on enones^{1,2}, we examine the reaction of these dipoles (**2**)³ towards 3-arylidene-4-isothiochromanones (**1**). These dipolarophiles (**1**) were synthesized by an acidic condensation of aromatic aldehydes with the isothiochromanone⁴.

The cycloaddition reactions occur very easily and yield (77-90%) regiospecifically the cycloadducts (**3**) which, by a treatment (r.t), with a trace of trifluoroacetic acid in chloroformic solution lead quantitatively to the 1,2,4-triphenyl-4,10-dihydro-10-thia-3,4-diazaphenanthrene derivatives (**4**) (Scheme and Table).

The regiochemistry of the cycloadducts (**3**), namely 1,3,4-triaryl-spiropyrazoline[5:3']4'-isothiochromanones, was established by ¹³C n.m.r. spectroscopy : $\delta C^{5:3'}$ = 80.13 to 80.74 ppm (singlet, CDCl₃/TMS). These chemical shift values were in good agreement with that one of a quaternary carbon atom bounded at once with a sulfur and a nitrogen atom.⁵

The elemental analyses of the products (**4**) showed the loss of a water molecule from the corresponding compounds (**3**) and their infrared spectra did not exhibit a $\nu(C=O)$ band.

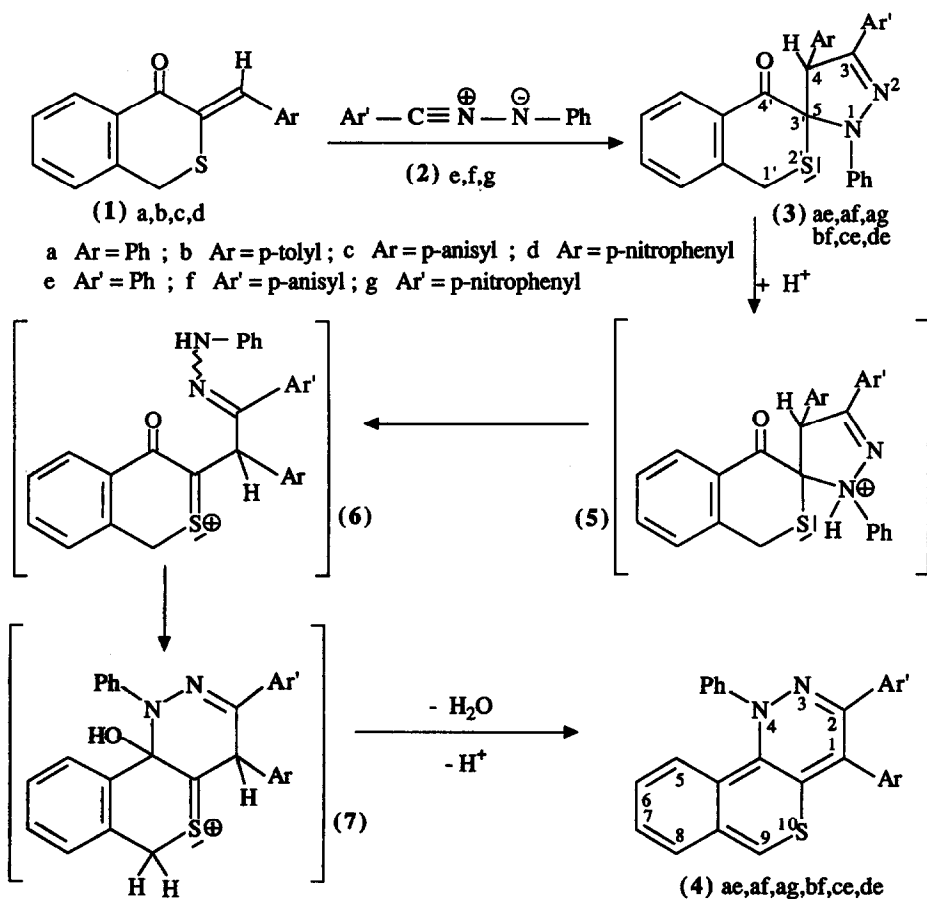
In the ¹³C n.m.r. spectra of the compounds (**4**) (CDCl₃), we observed the absence of the signals for sp³ aliphatic carbon atom (except those of the substituents of Ar and Ar') or for a carbonyl carbon atom. In the ¹H n.m.r. spectra, (CDCl₃/TMS), the singlet signal between 7.62 and 7.89 ppm for the H⁹ proton of compounds (**4**) is in good agreement with the proposed structure.

Since the cycloadducts obtained from 2-arylidene-1-tetralones were stable in an acidic medium², the part played by the sulfur atom in the evolution of the cycloadducts (**3**) is essential.

The acidic ring opening of the pyrazolinic cycle of (**3**) is followed by an intramolecular nucleophilic addition of the sp³ nitrogen atom of the intermediary hydrazone (**6**) on the carbonyl of the isothiochromanone moiety, and the reaction ended with the departure of a water molecule to give the product (**4**).

Moreover, the mass spectra of (**3ae**) and (**4ae**) were indistinguishable and so, under electronic impact (ei), or by chemical ionization mode (ci), compound (**3**) loses a water molecule to give (**4**). The molecular ion, ei : M⁺ (m/e = 428) or ci : (M+1)⁺ (m/e = 429), is also the base peak of the spectrum, confirming the remarkable stability of this compound (**4**).

To the best of our knowledge, this is the first example of obtention of derivatives of this new heterocyclic class.



Compound	Ar	Ar'	Yield %	mp °C	$\delta_{C^{5:3}}$ (3) ^a ppm	δ_{H^9} (4) ^a ppm
(3ae)	phenyl	phenyl	84	160	80.25	-
(3af)	"	p-anisyl	84	203	80.42	-
(3ag)	"	p-nitrophenyl	82	177	80.22	-
(3bf)	p-tolyl	p-anisyl	85	162	80.13	-
(3ce)	p-anisyl	phenyl	90	194	80.39	-
(3de)	p-nitrophenyl	"	77	130	80.74	-
(4ae)	phenyl	"	97	214	-	7.89
(4af)	"	p-anisyl	98	194	-	7.65
(4ag)	"	p-nitrophenyl	97	148	-	7.70
(4bf)	p-tolyl	p-anisyl	95	165	-	7.62
(4ce)	p-anisyl	phenyl	98	219	-	7.68
(4de)	p-nitrophenyl	"	96	158	-	7.78

^a ¹H n.m.r. spectra were run at 200 MHz and ¹³C n.m.r. spectra were run at 50 MHz on a Bruker AC-200 spectrometer (Solvent CDCl₃/TMS).

References

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