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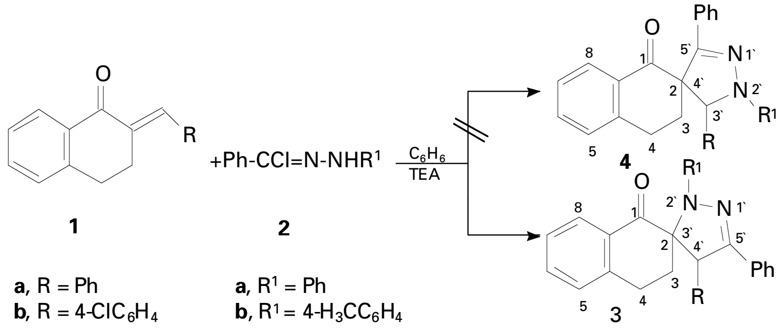
Regioselective synthesis of spiro[naphthalene-2(1*H*),3′-[3*H*]pyrazol]-1-ones utilizing 1,3-dipolar cycloaddition of nitrilimines

Nawal Mishriky[a]*, Adel S. Girgis[a] and Yehia A. Ibrahim[b]

[a]*National Research Centre, Dokki, Cairo, Egypt*
[b]*Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt*

1,3-Dipolar cycloaddition reaction of nitrilimines to a variety of 2-arylmethylidene-3,4-dihydro-1-naphthalenones **1a–h** afforded the corresponding spiro[naphthalene-2(1*H*),3′-[3*H*]pyrazol]-1-ones **3** and not the isomeric spiro[naphthalene-2(1*H*),4′-[4*H*]pyrazol]-1-ones **4**, in high regioselectivity. The structure of the isolated products was established through different spectroscopic techniques and confirmed *via* HMBC.

The concept of 1,3-dipolar cycloaddition has been well utilized in the synthesis of a number of heterocyclic compounds by a one-pot process.[1,2] Many investigations were also directed towards cycloaddition of nitrilimines to exocyclic double bond bearing compounds. This phenomenon is considered a very successful process for the construction of many spiro-compounds.[18–23] In the present work, it is intended to explore the reaction of nitrilimines with exocyclic double bond of arylidenes derived from 1,2,3,4-tetrahydro-1-naphthalenone in order not only to isolate the corresponding spiro-heterocyclic compounds but also to study the regioselectivity of the reaction.



a, R = Ph
b, R = 4-ClC$_6$H$_4$
c, R = 4-FC$_6$H$_4$
d, R = 4-H$_3$CC$_6$H$_4$
e, R = 4-H$_3$COC$_6$H$_4$
f, R = 4-(CH$_3$)$_2$NC$_6$H$_4$
g, R = 2-thienyl
h, R = 2-furanyl

a, R^1 = Ph
b, R^1 = 4-H$_3$CC$_6$H$_4$

	R	R^1
a	Ph	Ph
b	Ph	4-H$_3$CC$_6$H$_4$
c	4-ClC$_6$H$_4$	Ph
d	4-ClC$_6$H$_4$	4-H$_3$CC$_6$H$_4$
e	4-FC$_6$H$_4$	Ph
f	4-FC$_6$H$_4$	4-H$_3$CC$_6$H$_4$
g	4-H$_3$CC$_6$H$_4$	Ph
h	4-H$_3$CC$_6$H$_4$	4-H$_3$CC$_6$H$_4$
i	4-H$_3$CO-C$_6$H$_4$	Ph
j	4-H$_3$CO-C$_6$H$_4$	4-H$_3$CC$_6$H$_4$
k	4-(CH$_3$)$_2$NC$_6$H$_4$	Ph
l	2-thienyl	Ph
m	2-thienyl	4-H$_3$CC$_6$H$_4$
n	2-furanyl	Ph
o	2-furanyl	4-H$_3$CC$_6$H$_4$

Fig. 1

Reaction of 2-arylmethylidene-3,4-dihydro-1-naphthalenones **1a–h** with nitrilimines (generated *in situ* by triethylamine dehydrohalogenation of the corresponding hydrazonoyl halides **2a,b**) in refluxing dry benzene, afforded only one regio-isolable isomer. The structure of which was established to be **3** rather than **4** based on spectroscopic and analytical data. The ^{1}H-NMR spectra of **3a–o** reveal the presence of a singlet signal at 4.69–5.17 ppm assignable for the pyrazole H-4′.[24-28] The appearance of this signal ruled out the presence of the other regio-isomer **4** which is expected to exhibit its signal at a chemical shift (δ) value downfield than 5.6 ppm.[26] ^{13}C-NMR of **3a** as a representative example add a good support for the proposed structure, where the spectrum exhibits the presence of C-3′ and C-4′ (spiro carbon) at 76.2, 60.5 ppm respectively, in accord with chemical shift values of similar structures.[27]

A conclusive evidence for the proposed structure was received through heteronuclear multi-bond connectivity 2D-NMR technique (HMBC) of **3a** as a representative example (see Fig. 1.). Where, the spectrum exhibits just one correlation between the pyrazole C-5′ (C=N at 148.2 ppm) and H-4′ (at 4.78 ppm) *via* $^2J_{CH}$. However, the pyrazole C-4′ (at 60.5 ppm) exhibits a connectivity with the naphthalenone H-3 (at 2.97 ppm) *via* $^3J_{CH}$. If the structure of **4** has any existence, strong correlations between the pyrazole C-5′ (C=N) and both the pyrazole H-3′ and naphthalenone H-3 must be appeared *via* $^3J_{CH}$ in both cases.

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* To receive any correspondence.

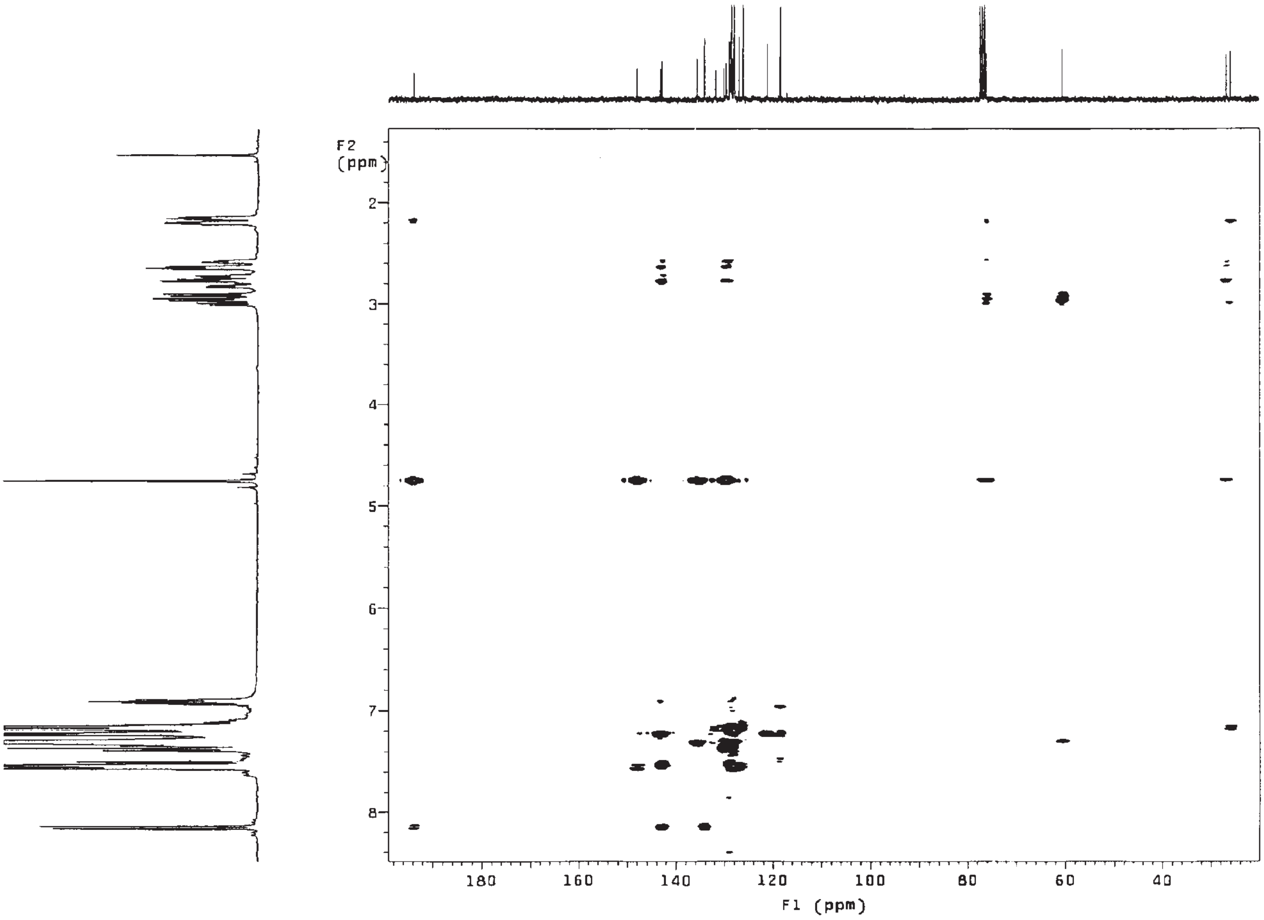

Fig. 2

Attempts for either isolation or identification of the other regioisomer **4** from the reaction mother liquor were unsuccessful.

Techniques used: Elemental analyses, IR, ^{1}H-NMR, ^{13}C-NMR, 2D-HMBC.

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