Revue Roumaine de Chimie, **2006**, *51*(4), 255–260

Dedicated to Professor Dr. ALEXANDRU T. BALABAN, member of the Roumanian Academy on the occasion of his 75th anniversary

NEW PYRAZOLES BY 1,3-DIPOLAR CYCLOADDITION REACTIONS BETWEEN SYDNONES AND ACTIVATED ALKYNES

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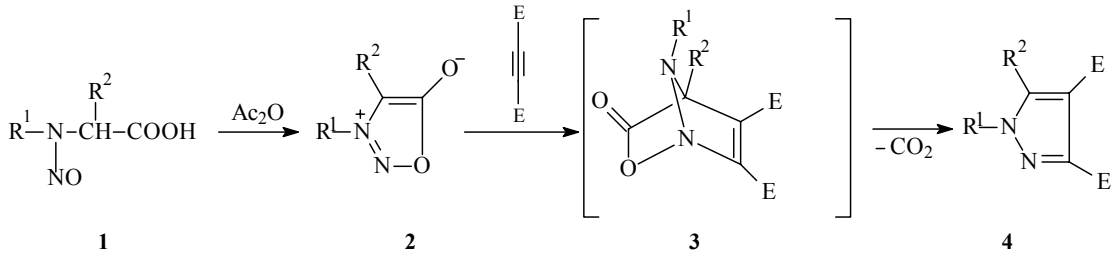
Received October 14, 2005

The 3-(2,4-dimethylphenyl)sydnone(**8a**) was halogenated at the 4-position giving 4-halogenosydnones **8b-d**. The 1,3-dipolar cycloaddition reactions of sydnones **8** with symmetrical and non-symmetrical acetylenic esters afforded pyrazoles **9a-g**, **10a,b** and **11**, respectively. The variation of the ^{13}C-NMR chemical shifts for the endocyclic carbons in the sydnone and pyrazole ring correlated with the nature of the halogen atom was determined.

INTRODUCTION

Sydnones **2** are dipolar heteroaromatic members of the general class of mesoionic compounds.[1-5] Numerous sydnone derivatives have been found to possess unique pharmacological activities. Sydnones can be readily prepared by cyclodehydration of *N*-substituted-*N*-nitrozo-aminoacids **1** with reagents such as acetic anhydride. The resulting compounds are nonbenzenoid heterocyclic aromatic five-membered rings and possess some unusual characteristics. They can be regarded as mesoionics systems with positive and negative charges distributed around the ring depending on their resonance forms. Sydnones undergo smooth cycloaddition with acetylenes to give pyrazoles **4** in high yield.[3-10] The reaction involves a 1,3-dipolar cycloaddition of the sydnones to the corresponding acetylene followed by carbon dioxide evolution and aromatization.



1 **2** **3** **4**

Scheme1

The present work describes the synthesis of 4-R-(2,4-dimethylphenyl)sydnones **8a-d** (R = H, Cl, Br, I) and their cycloaddition reactions with acetylenic esters to form new pyrazoles **9a-e, 10a,b** and **11**, respectively.

RESULTS AND DISCUSSION

The starting material for the preparation of sydnones and pyrazoles was *N*-(2,3-dimethylphenyl)glycine (**6**), obtained by a slight modification of the method described in the literature for this compound.[11] The 4-unsubstituted sydnone **8a** was prepared in good yield from acid **6** by nitosation and subsequent cyclization of

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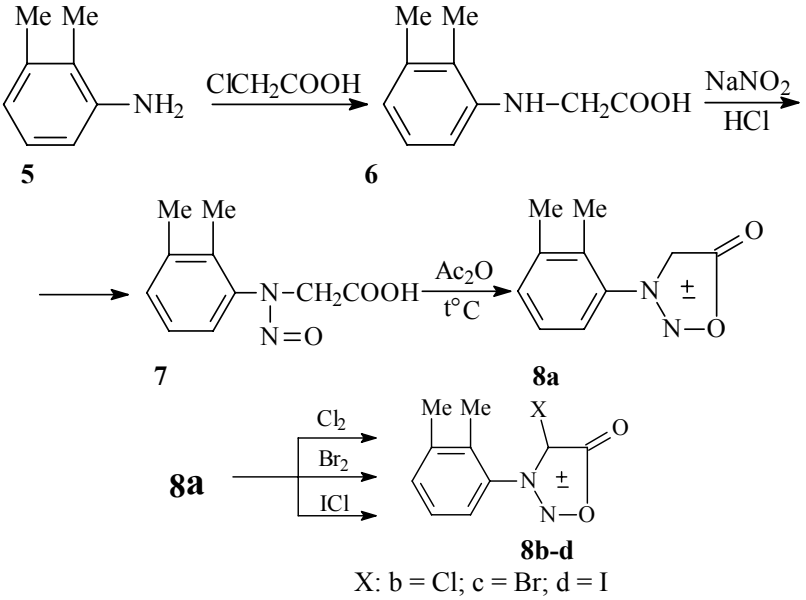
the nitroso derivative **7**. The transformation of nitrosoacid into sydnone was achieved with acetic anhydride in the presence of a catalytic amount of pyridine (Scheme 2).

Sydnones unsubstituted at the 4-position display halogenation reaction such as chlorination, bromination and iodination. The chlorination and bromination of sydnone **8a** were performed with chlorine- and bromine-acetic acid to give 4-chloro- (**8b**) and 4-bromosydnone (**8c**), respectively. Sydnone **8a** was iodinated in good yield with the reagent iodine monochloride[12-14] in acetic acid medium in the presence of sodium acetate (Scheme 2).



Scheme 2

The structure of sydnones **8a-d** was confirmed by elemental analysis and NMR spectroscopy. The variation of the ^{13}C-NMR chemical shifts for the endocyclic carbons in the sydnone ring correlated with the nature of the halogen atom was determined (Table 1). The ^{13}C-NMR spectra of 4-iodo and 4-chlorosydnones showed negative increments at C-4, whereas 4-chlorosydnone showed a positive increment. A weak influence on the polarization of the carbonyl group could be also observed with bromine and chlorine as substituents (Table 1).

Table 1

^{13}C-NMR chemical shifts for the endocyclic carbons in the sydnone ring

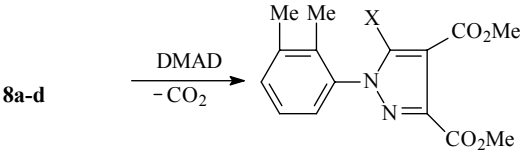
X	H	Cl	Br	I
C-4(δ)	97.0	100.3	85.7	52.6
Δδ	0	+3.3	-11.3	-44.4
C-5(δ)	168.7	163.7	165.4	168.7
Δδ	0	-5.1	-3.4	0

The 1,3-dipolar cycloaddition reaction between sydnones **8a-d** and dimethylacetylenedicarboxylate (DMAD) gave the corresponding pyrazoles **9a-d**. Similarly, the reaction of sydnone **8a** and di(2,2,2-trifluoroethyl) acetylenedicarboxylate gave pyrazole **9e** (Scheme 3).

The pyrazoles **9a-e** were characterized by elemental analysis and NMR spectroscopy.

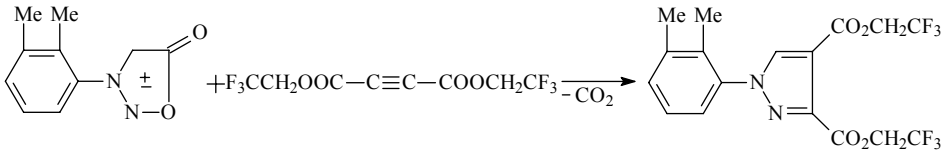
In the ^{1}H-NMR spectra of pyrazole **9e** the methylene protons of trifluoroethyl groups appeared as two quartets (J = 8.3 Hz) due to the F/H couplings.

In ^{13}C-NMR spectra the trifluoromethyl groups in pyrazole **9e** appear as two quartets with coupling constants of J = 278.2 Hz. Also, the methylene carbons of the trifluoroethyl groups show two quartets with coupling constants of 36.9 Hz.



8a-d **9a-d**

X: a = H; b = Cl; c = Br; d = I



8a **9e**

Scheme 3

The ^{13}C-NMR spectra of 5-iodopyrazole **9d** showed about the same increments for the signal of C-5 as in the case of the corresponding 4-iodosydnone **8d**. The ^{13}C-NMR data of the new pyrazoles are close to those reported in the literature.[15]

Table 2

^{13}C-NMR data for the carbon atoms of pyrazoles **9a-d**

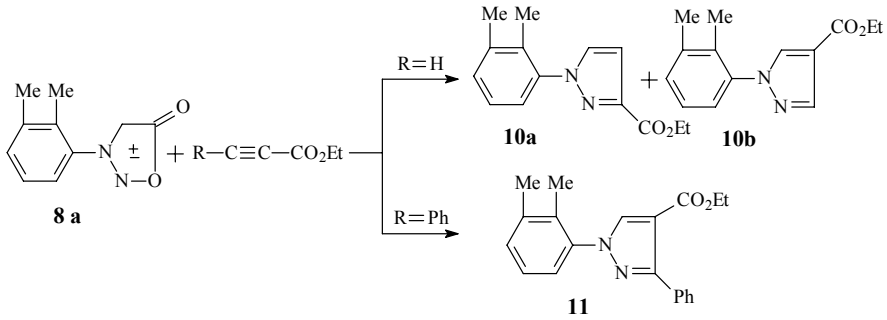
X	H	Cl	Br	I
C-5 (δ)	135.9	132.7	115.3	91.0
Δδ	0	-3.2	-20.6	-44.9
C-4 (δ)	115.3	112.2	119.7	120.6
Δδ	0	-3.1	+ 4.4	+ 5.3
C-3 (δ)	143.7	143.7	144.2	145.0
Δδ	0	0.0	+ 0.5	+ 1.3

The 1,3-dipolar cycloaddition reaction between sydnone **8a** and non-symmetrical alkynes was also investigated. Sydnone **8a** and ethyl propiolate gave a mixture of two regioisomers **10a** and **10b** (Scheme 4).

The ratio between the two regioisomers was established by ^{1}H-NMR spectroscopy and was found to be 3:1 (**10a**:**10b**). In the ^{1}H-NMR spectrum, the major isomer **10a** exhibits two doublets (J = 2,2 Hz) for H-4 and H-5 protons, whereas in the compound **10b** the atoms H-3 and H-5 appear as two singlets (Scheme 4).

Treatment of sydnone **8a** with ethyl phenylpropiolate in xylene at reflux gave regiospecifically 4-carboethoxy-1-(2,3-dimethylphenyl)-3-phenylpyrazole **11**. The structure of pyrazole **11** was assigned by NMR spectroscopy. The observed reactivity of the acetylenic compounds towards sydnone **8a** has the following order: $MeO_2CC{\equiv}CCO_2Me$ > $HC{\equiv}CCO_2Et$ > $PhC{\equiv}CCO_2Et$.

The above results were in good accordance with the literature data concerning 1,3-dipolar cycloaddition between sydnones and non-symmetrical alkynes.[6-10]



8 a **10a** **10b** **11**

Scheme 4

CONCLUSIONS

The 3-(2,4-dimethylphenyl)sydnone (**8a**) was halogenated at the 4-position giving 4-halogenosydnones **8b-d**.

The 1,3-dipolar cycloaddition reactions of sydnones **8** with symmetrical and non-symmetrical acetylenic esters gave pyrazoles **9a-e**, **10a,b** and **11**, respectively.

The structure of the new compounds was assigned by elemental analysis and NMR spectroscopy. Also, the variation of the ^{13}C-NMR chemical shifts for the endocyclic carbons in the sydnone and pyrazole ring correlated with the nature of the halogen atom was determined.

EXPERIMENTAL

Melting points were determined on a Boetius hot plate and are uncorrected. The NMR spectra were recorded on a Varian Gemini 300 BB instrument, operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C.

*N-(2,3-Dimethylphenyl)glycine **(6)***

30 mL (30.2 g; 0.25 mol) 2,3-dimethylaniline, 18.6 g (0.2 mol) monochloroacetic acid, 20 mL ethanol and 300 mL water were refluxed for 3 hrs. The reaction mixture was cooled in a water-ice bath and the precipitate was filtered by suction and then was washed with water on the filter. After drying the product was triturated with benzene and filtered off. Yield 57% (based on the monochloroacetic acid); m.p. 173-175^{0}C (lit.[10] 176^{0}C). The crude product was pure enough to be used in the next step.

^{1}H-NMR ($CDCl_3$+TFA, δ, ppm; *J*, Hz): 2.30 (s, 1H, 2'-Me); 2.33 (s, 1H, 3'-Me); 4.23 (s, 2H, CH_2); 7.20-7.32 (m, 3H, H-4', H-5', H-6').

^{13}C-NMR ($CDCl_3$+TFA, δ, ppm): 12.9 (2'-Me); 20.1 (3'-Me); 52.0 (CH_2); 120.3; 127.5; 132.2 (C-4', C-5', C-6'); 129.2; 132.8 (C-2', C-3'); 140.5 (C-1'); 168.7 (CO).

*3-(2,3-Dimethylphenyl)sydnone(**8a**)*[16]

To a solution of 2 g NaOH in 30 mL of water were added 3.6 g (20 mmol) *N*-(2,3-dimethylphenyl)glycine and 1.4 g (21 mmol) of $NaNO_2$. In the cooled solution 10 mL of HCl were dropped under stirring, the temperature maintained below 5°C. The nitroso derivative which separated as an oil was extracted twice with CH_2Cl_2. The organic layer was dried on $CaCl_2$ and then the solvent was evaporated off. The residue was treated with 30 mL of acetic anhydride and 2 mL of pyridine and evaporated under reduced pressure on the water bath. Yield 78%; m.p. 135-137^{0}C (from isopropanol). Found: C, 63.40; H, 5.62; N, 15.01; $C_{10}H_{10}N_2O_2$ requires: C, 63.09; H, 5.26; N, 14.72.

^{1}H-NMR ($CDCl_3$, δ, ppm; *J*, Hz): 2.17 (s, 3H, 2'-Me); 2.40 (s, 3H, 3'-Me); 6.48 (s, 1H, H-4) 7.25 (dd, 1H, 7,8; 1,5; H-4'); 7.32 (t, 1H, 7,8; H-5'); 7.45 (dl, 1H, 7,8; H-6').

^{13}C-NMR ($CDCl_3$, δ, ppm): 13.8 (2'-Me); 20.2 (3'-Me); 97.4(C-4); 122.7 (C-6'); 126.6 (C-4'); 131.8 (C-2'); 133.3 (C-5'); 134.1 (C-3'); 139.6 (C-1'); 168.7 (CO).

*3-(2,3-Dimethylphenyl)-4-chlorosydnone**(8b)***

To a suspension of 1.9 g (10 mmol) sydnone and 1 g dry sodium acetate dissolved in 15 mL glacial acetic acid was added dropwise with stirring and cooling 0.71g (10 mmol) of chlorine dissolved in 15 mL glacial acetic acid. After 20 min. the reaction mixture was poured into water and the precipitate filtered off by suction. Yield 79%; m.p. 126-128^{0}C (from ethanol). Found: C, 53.70; H, 4.31; Cl, 16.05; N, 12.69; $C_{10}H_9ClN_2O_2$ requires: C, 53.43; H, 4.01; Cl, 15.78; N, 12.47.

^{1}H-NMR ($CDCl_3$, δ, ppm; *J*, Hz): 2.12 (s, 3H, 2'-Me); 2.42 (s, 3H, 3'-Me); 7.21 (dd, 1H, 7,8; 1,5; H-4'); 7.36 (t, 1H, 7,8; H-5'); 7.49 (dl, 1H, 7,8; H-6').

^{13}C-NMR ($CDCl_3$, δ, ppm): 13.9 (2'-Me); 20.2 (3'-Me); 100.3 (C-4); 123.5 (C-6'); 126.9 (C-4'); 132.1 (C-2'); 132.8 (C-3'); 133.9 (C-5'); 139.7 (C-1'); 163.7 (CO).

*3-(2,3-Dimethylphenyl)-4-bromosydnone**(8c)***

To a suspension of 1.9 g (10 mmol) sydnone and one gram dry sodium acetate was added dropwise with stirring and cooling 1.76 g (0.56 mL, 11 mmol) of bromine dissolved in 15 mL glacial acetic acid. After 15 min. 4-bromosydnone was precipitated by the addition of water. The product was filtered off and thoroughly washed with water. Yield 85%; m.p. 140-142°C (from isopropanol). Found: C, 44.88; H, 3.61; Br, 30.35; N, 10.67; $C_{10}H_9BrN_2O_2$ requires: C, 44.59; H, 3.34; Br, 26.69; N, 10.40.

^{1}H-NMR ($CDCl_3$, δ, ppm; *J*, Hz): 2.10 (s, 3H, 2'-Me); 2.42 (s, 3H, 3'-Me); 7.19 (dd, 1H, 7,8; 1,5; H-4'); 7.36 (t, 1H, 7,8; H-5'); 7.48 (dl, 1H, 7,8; H-6').

^{13}C-NMR ($CDCl_3$, δ, ppm): 13.9 (2'-Me); 20.2 (3'-Me); 85.7(C-4); 123.6(C-6'); 126.8 (C-4'); 132.7 (C-2'); 133.0 (C-3'); 133.8 (C-5'); 139.7 (C-1'); 165.4 (CO).

*3-(2,3-Dimethylphenyl)-4-iodosydnone**(8d)***

A solution of 3.9 g (24 mmol) of iodine monochloride in 15 mL of glacial acetic acid was added dropwise to a stirred mixture of 3.8 g (20 mmol) of sydnone and 2.6 g (31 mmol) of dry sodium acetate in 20 mL glacial acetic acid. Stirring was continued for 1

hr at 50°C, after which the 4-iodosydnone was precipitated by addition of water. The product was filtered off and thoroughly washed with water. Yield 87%; m.p. 145-147^{0}C (from ethanol). Found: C, 38.22; H, 3.11; I, 40.45; N, 9.12; $C_{10}H_9IN_2O_2$ requires: C, 37.97; H, 2.85; I, 40.19; N, 8.86.

^{1}H-NMR ($CDCl_3$, δ, ppm; *J*, Hz): 2.07 (s, 3H, 2'-Me); 2.42 (s, 3H, 3'-Me); 7.15 (dd, 1H, 7,8; 1,5; H-4'); 7.35 (t, 1H, 7,8; H-5'); 7.47 (dl, 1H, 7,8; H-6').

^{13}C-NMR ($CDCl_3$, δ, ppm): 13.9 (2'-Me); 20.2 (3'-Me); 52.6 (C-4); 123.6 (C-6'); 126.8 (C-4'); 132.6 (C-2'); 134.4 (C-3'); 133.7 (C-5'); 139.6 (C-1'); 168.7 (CO).

Synthesis of 3,4-dicarbomethoxy pyrazoles. General procedure:

A mixture of 10 mmol sydnone (**8a-d**) and 1,7 g (1,6 mL; 12 mmol) of DMAD was refluxed in 20 mL toluene for 10 hrs. After removal of the solvent in vacuum, pyrazole was obtained as oil which crystallized on cooling.

*3,4-Dicarbomethoxy-1-(2,3-dimethylphenyl)pyrazole(**9a**)*

Yield 89%; m.p. 116-118°C (from isopropanol). Found: C 62.77; H 5.81; N 9.90; $C_{15}H_{16}N_2O_4$ requires: C 62.45; H 5.55; N 9.71.

^{1}H-NMR ($CDCl_3$, δ, ppm, *J*, Hz): 2.05 (s, 3H, 2'-CH_3); 2.34 (s, 3H, 3'-CH_3); 3.88; 3.97 (2s, 6H, OCH_3); 7.16 (dd, 1H, 7,9; 1,4; H-4'); 7.20 (t, 1H, 7,9; H-5'); 7.30 (dl, 1H, 7,9; H-6'); 8.05 (s, 1H, H-5).

^{13}C-NMR ($CDCl_3$, δ, ppm): 14.2 (2'-**C**H_3); 20.2 (3'-**C**H_3); 51.9; 52.5 (O**C**H_3); 115.3 (C-4); 124.1 (C-6'); 126.0 (C-4'); 131.2 (C-5'); 132.8 (C-2'); 135.9 (C-5); 138.5; 138.6 (C-1', C-3'); 143.7 (C-3); 161.9; 162.0 (CO).

*3,4-Dicarbomethoxy-5-chloro-1-(2,3-dimethylphenyl)pyrazole(**9b**)*

Yield 76%; m.p. 64-66^{0}C (from isopropanol). Found: C 56.03; H 4.93; Cl 11.32; N 8.93; $C_{15}H_{15}ClN_2O_4$ requires: C 55.78; H 4.65; Cl 10.98; N 8.67.

^{1}H-NMR ($CDCl_3$, δ, ppm, *J*, Hz): 1.94 (s, 3H, 2'-**C**H_3); 2.35 (s, 3H, 3'-**C**H_3); 3.94; 3.96 (2s, 6H, OCH_3); 7.12 (dd, 1H, 7,7; 1,4; H-4'); 7.23 (t, 1H, 7,7; H-5'); 7.33 (dl, 1H, 7,7; H-6')

^{13}C-NMR ($CDCl_3$, δ, ppm): 14.0 (2'-**C**H_3); 20,1 (3'-**C**H_3); 52.3; 52.7 (O**C**H_3); 112.2 (C-4); 125.3 (C-6'); 126.1 (C-4'); 132.0 (C-5'); 132.7 (C-5); 134.5 (C-2'); 136.9 (C-3'); 138.6 (C-1'); 143.7 (C-3); 161.4; 161.5 (CO).

*3,4-Dicarbomethoxy-5-bromo-1-(2,3-dimethylphenyl)pyrazole(**9c**)*

Yield 75%; m.p. 83-85^{0}C (from ethanol). Found: C 55.29; H4.33; Br 22.02; N 7.90; $C_{15}H_{15}BrN_2O_4$ requires: C 45.02; H 4.08; Br 21.76; N 7.63.

^{1}H-NMR ($CDCl_3$, δ, ppm, *J*, Hz): 1.89 (s, 3H, 2'-CH_3); 2.32 (s, 3H, 3'-CH_3); 3.92; 3.94 (2s, 6H, OCH_3); 7.08 (dd, 1H, 7,6; 1,3; H-4'); 7.20 (t, 1H, 7,6; H-5'); 7.30 (dl, 1H, 7,6; H-6').

^{13}C-NMR ($CDCl_3$, δ, ppm): 14.0 (2'-**C**H_3); 20.1 (3'-**C**H_3); 52.3; 52.6 (O**C**H_3); 115.3 (C-5); 119.7 (C-4); 125.4 (C-6'); 126.0 (C-4'); 131.9 (C-5'); 134.5 (C-2'); 136.9 (C-3'); 138.5 (C-1'); 144.2 (C-3); 161.3; 161.7 (CO).

*3,4-Dicarbomethoxy-5-iodo-1-(2,3-dimethylphenyl)pyrazole(**9d**)*

Yield 77%; 108-110^{0}C (from isopropanol). Found: C 43.71; H 3.62; I 31.03; N, 6.99; $C_{15}H_{15}IN_2O_4$ requires: C 43.48; H 3.62; I 30.68; N 6.76.

^{1}H-NMR ($CDCl_3$, δ, ppm, *J*, Hz): 1.88 (s, 3H, 2'-**C**H_3); 2.35 (s, 3H, 3'-**C**H_3); 3.94; 3.95 (2s, 6H, OCH_3); 7.08 (dd, 1H, 7,6; 1,3; H-4'); 7.22 (t, 1H, 7,6; H-5'); 7.33 (dl, 1H, 7,6; H-6').

^{13}C-NMR ($CDCl_3$, δ, ppm): 14.2 (2'-**C**H_3); 20.2 (3'-**C**H_3); 52.3; 52.6 (O**C**H_3); 91.0 (C-5); 120.6 (C-4); 125.7 (C-6'); 126.0 (C-4') ; 131.8 (C-5',); 134.6 (C-2'); 138.5; 138.6 (C-1', C-3'); 145.0 (C-3); 161.4; 162.3 (CO).

*Di(2,2,2-trifluoroethyl) ester, 1-(2,3-dimethylphenyl)pyrazole-3,4-dicarboxylic acid(**9e**)*

1.45 g (5 mmol) sydnone (**8a**) and 1.7 g (6 mmol) of di(2,2,2-trifluoroethyl) acetylenedicarboxylate were refluxed in 20 mL toluene for 12 hrs. After removal of the solvent in vacuum, pyrazole was obtained as oil which crystallized on cooling. Yield 83%; m.p. 108-110°C (ethanol).Found: C 62.77; H 5.81; N 9.90; $C_{15}H_{16}N_2O_4$ requires: C 62.45; H 5.55; N 9.71.

^{1}H-NMR ($CDCl_3$, δ, ppm, *J*, Hz): 2.00 (s, 3H, 2'-CH_3); 2.28 (s, 3H, 3'-CH_3); 4.59; 4.68 (2q, 4H, 8.3, CH_2); 7.10 (dd, 1H, 7.8; 1.9; H-4'); 7.14 (t, 1H, 7.8; H-5'); 7.24 (dd, 1H, 7.9; 1.9, H-6'); 8.08 (s, 1H, H-5).

^{13}C-NMR ($CDCl_3$, δ, ppm; *J*, Hz): 14.3 (2'-CH_3); 20.3 (3'-CH_3); 60.6; 61.1 (2q, 36.9, 2**C**H_2); 114.0 (C-4); 122.8 (2q, 278.2, 2CF_3) 124.1 (C-6'); 126.2 (C-4'); 131.2 (C-5'); 132.8 (C-2'); 136.7 (C-5); 138.5; 138.6 (C-1', C-3'); 142.7 (C-3); 159.3; 159.8 (2CO).

*3-Carboethoxy-1-(2,3-dimethylphenyl)pyrazole(10a) and 4-carboethoxy-1-(2,3-dimethylphenyl)pyrazole**(10b)***

1.9 g (10 Mmol) 3-(2,3-dimethylphenyl) sydnone and 1.3 mL (13 mmol) ethyl propiolate were refluxed in 20 mL xylene for 12 hrs. The solvent was evaporated in vacuum and the crude oil was purified by chromatography on column eluted with dichloromethane. The ratio between two regioisomers was determined by NMR spectroscopy and was found to be 3:1. The major isomer **10a** was obtained as white crystals with m.p. 62-64°C by crystallization from ethanol. Found: C 69.11; H 6.94; N 11.72; $C_{14}H_{16}N_2O_2$ requires: C 68.83; H 6.60; N 11.47.

*3-Carboethoxy-1-(2,3-dimethylphenyl)pyrazole**(10a)***

^{1}H-NMR ($CDCl_3$; δ, ppm; *J*, Hz): 1.40 (t, 3H, 7.1; CH_3CH_2); 2.01 (s, 3H, 2'-CH_3); 2.32 (s, 3H, 3'-CH_3); 4.42 (q, 2H, 7.1; CH_2); 6.98 (d, 1H, 2.4; H-4); 7.15-7.26 (m, 3H, H-4', H-5', H-6'); 7.56 (d, 1H, 2,4; H-5).

^{13}C-NMR ($CDCl_3$, δ, ppm): 14.1; 14.4 (2'-CH_3; $CH_2\underline{CH_3}$); 20.2 (3'-CH_3); 60.9 (CH_2O); 109.0 (C-4); 124.3; 125.7 (C-4', C-6'); 130.6 (C-5'); 132.4 (C-5); 133.0 (C-1'); 138.4; 139.6 (C-2', C-3'); 144.5 (C-3); 162.4 (CO).

*4-Carboethoxy-1-(2,3-dimethylphenyl)pyrazole**(10b)**.*

^{1}H-NMR ($CDCl_3$; δ, ppm; *J*, Hz): 1.33 (t, 3H, 7.1; CH_3CH_2); 2.02 (s, 3H, 2'-CH_3); 2.34 (s, 3H, 3'-CH_3); 4.30 (q, 2H, 7,1; CH_2); 7.12-7.26 (m, 3H, H-4', H-5', H-6'); 8.02 (s, 1H, H-5); 8.07 (s, 1H, H-3)..

^{13}C-NMR ($CDCl_3$; δ, ppm): 14.1; 14.4 (2'-CH_3; $CH_2\underline{CH_3}$); 20.2 (3'-CH_3); 60.2 (CH_2O); 115.7 (C-4); 124.0; 125.9 (C-4', C-6'); 130.6 (C-5'); 132.7 (C-1'); 134.1 (C-5); 138.5; 139.4 (C-2', C-3'); 141.4 (C-3); 162.6 (CO).

*4-Carboethoxy-3-phenyl-1-(2,3-dimethylphenyl)pyrazole**(11)***

1.9 g (10 Mmol) 3-(2,3-dimethylphenyl)sydnone and 1.9 mL (2 g, 11.5 mmol) ethyl phenylpropiolate were refluxed in 20 mL xylene for 24 hrs. The solvent was evaporated in vacuum and the crude oil was purified by chromatography on column eluted with dichloromethane. The pyrazole **11** was obtained as white crystals with m.p. 62-63°C by crystallization from ethanol. Found: C 75.11; H 6.60; N 9.02; $C_{20}H_{20}N_2O_2$ requires: C 74.98; H 6.29; N 8.74.

^{1}H-NMR ($CDCl_3$, δ, ppm, *J*, Hz): 1.29 (t, 3H, 7,1; $\underline{CH_3}CH_2$); 2.14 (s, 3H, 2'-CH_3); 2.35 (s, 3H, 3'-CH_3); 4.29 (q, 2H, 7,1; CH_2); 7.17-7.28 (m, 3H, H-4', H-5', H-6'); 7.36-7.45 (m, 3H, *m*-Ph, *p*-Ph); 7.85-7.88 (m, 2H, *o*-Ph); 8.14 (s, 1H, H-5).

^{13}C-NMR ($CDCl_3$, δ, ppm): 14.2; 14.4 (2'-CH_3; $CH_2\underline{CH_3}$); 20.3 (3'-CH_3); 60.2 (CH_2O); 112.3 (C-4); 124.0; 125.9 (C-4', C-6'); 127.7; 129.3 (C-2, C-3, C-5, C-6, Ph); 128.4 (C-4, Ph); 130.6 (C-5'); 132.1 (C-1, Ph); 132.4 (C-1'); 136.5 (C-5); 138.6; 139.1 (C-2', C-3'); 153.3 (C-3); 163.1 (CO).

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