

Short Note

4,4'-[(2-Chlorophenyl)methylene]bis[1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-5-ol]

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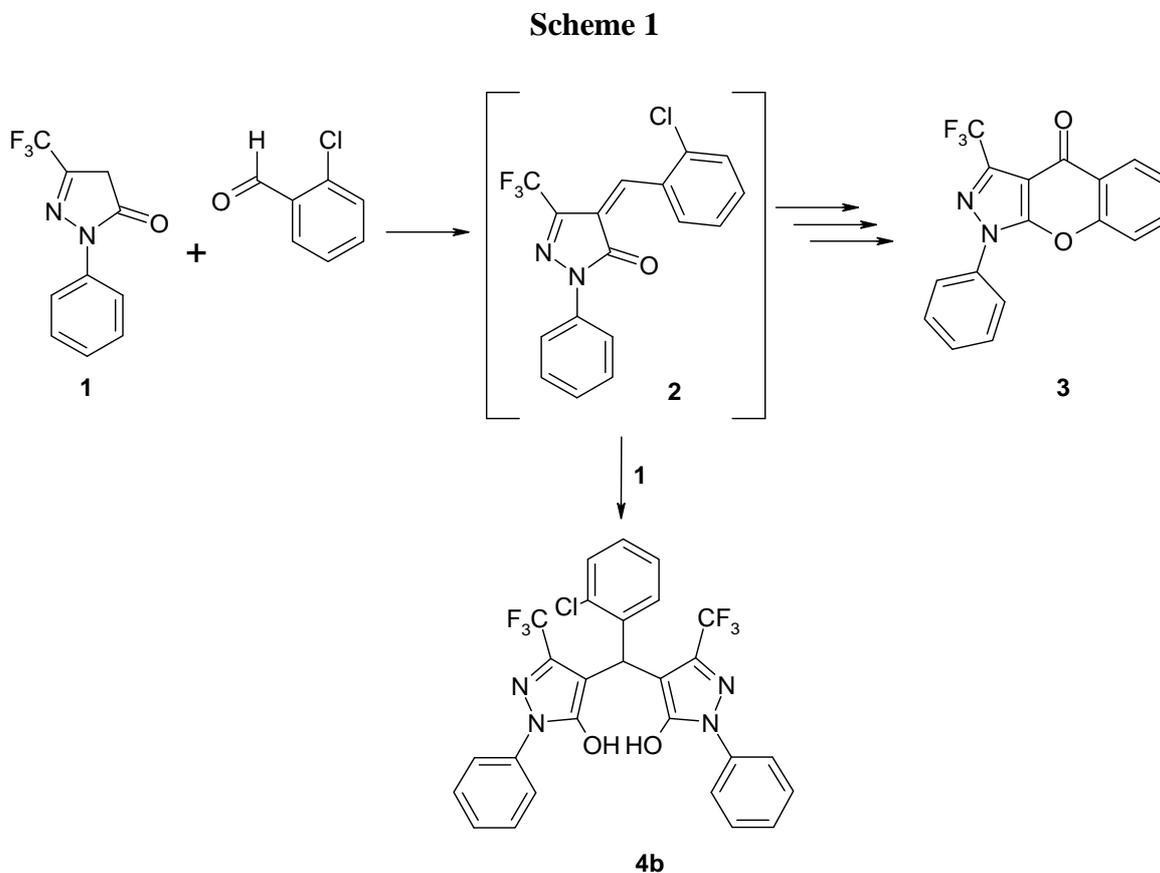
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Abstract: The reaction of 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one and 2-chlorobenzaldehyde leads to the title compound, which results from addition of a second pyrazolone unit to the primarily formed 1:1 condensation product. Detailed spectroscopic data (¹H NMR, ¹³C NMR, ¹⁹F NMR, IR, MS) are presented.

Keywords: 3-trifluoromethyl-2-pyrazolin-5-one; condensation; NMR spectroscopy

In the course of a synthetic program dedicated to the functionalization of 1-phenyl-3-trifluoromethyl-2-pyrazolin-5-one (**1**) [1] we were interested in compound **2**, which was considered as precursor in the synthesis of the chromeno[2,3-*c*]pyrazol-4(1*H*)-one **3** (Scheme 1). The synthesis of compounds similar to **2** has been described by *Sobahi* [2] and by *Zohdi* [3]: heating equimolar amounts of **1** and differently substituted benzaldehydes to 160 °C without a solvent resulted in the formation of the corresponding 1:1 condensation products [2]. However, when we applied such conditions (160 °C) in the reaction of **1** and 2-chlorobenzaldehyde we only obtained a product which – considering its characteristic spectroscopic data – turned out to be the 2:1 adduct **4b**. Obviously, the primarily formed 1:1 condensation product **2** instantly reacts with a second pyrazolone unit to afford dimer **4b**. Also the application of other reaction conditions (lower temperature, excess aldehyde, refluxing EtOH with catalytic amounts of piperidine) afforded **4b** as well. The formation of dimeric moieties similar to **4**

starting from **1** and substituted benzaldehydes upon heating in aqueous medium without a catalyst was recently reported by *Yao* and coworkers [4]. The structure of these products was unequivocally proved by X-ray structure analysis [4].



When we furthermore reacted **1** also with benzaldehyde and 2,4-dichlorobenzaldehyde, respectively, we obtained the corresponding dimeric compounds (**4a**, **4c**) as well (Figure 1). Melting points and ¹H-NMR spectroscopic data of the latter were in full agreement with those given by *Yao* [4].

The NMR spectra of compounds **4** exhibit the signals of the characteristic, central C(sp³)-H system (δ H: 5.22–5.68 ppm; δ C: 30.7–32.8 ppm; 1J : 124.5–128.0 Hz). For comparison reasons, the NMR spectroscopic data of the hitherto unknown title compound **4b** are presented together with those of known congeners **4a** and **4c** in Tables 1 and 2.

Experimental

Melting points were determined on a Reichert–Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV). IR spectrum: Perkin-Elmer FTIR Spectrum 1000 instrument (KBr-disc). The elemental analysis was performed at the Microanalytical Laboratory, University of Vienna. ¹H and ¹³C NMR spectra were recorded on a Varian UnityPlus 300 spectrometer at 28 °C (299.95 MHz for ¹H, 75.43 MHz for ¹³C). The centre of the solvent signal was used as an internal standard which was related to TMS with $\delta = 2.49$ ppm (¹H in DMSO-*d*₆) and $\delta = 39.5$ ppm (¹³C in DMSO-*d*₆). The digital resolutions were 0.2 Hz/data point in the ¹H and 0.4 Hz/data point in the ¹H-coupled ¹³C-NMR spectra (gated decoupling). ¹⁹F NMR spectra

(470.56 MHz) were obtained on a Bruker Avance 500 instrument with a ‘directly’ detecting broadband observe probe (BBFO) and were referenced using the absolute frequency scale (\mathcal{E} ratio). Unambiguous assignment of signals was accomplished using standard NMR techniques such as HSQC, HMBC, NOE-difference and fully ^1H -coupled ^{13}C -NMR (gated decoupling) [5].

Figure 1. Numbering of atoms in the representation of NMR spectra.

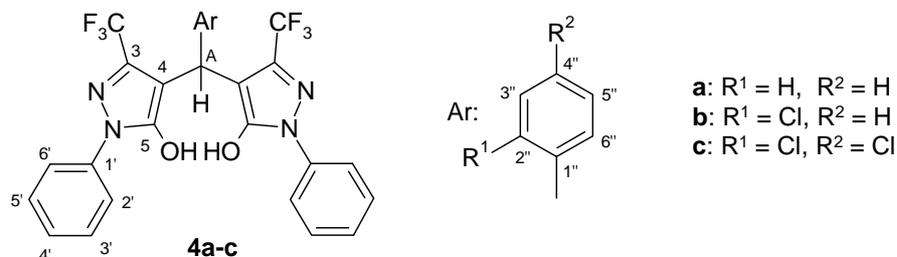


Table 1. ^1H -NMR and ^{19}F -NMR chemical shifts of compounds **4a-c** (δ , ppm, in DMSO- d_6).

comp.	OH	H _A	H of N-phenyl				H of aryl				^{19}F
			2',6'	3',5'	4'	2''	3''	4''	5''	6''	CF ₃
4a	8.33 ^a	5.22	7.87	7.41	7.23	7.26	7.26	7.12	7.26	7.26	-60.2
4b	6.88 ^a	5.68	7.82	7.42	7.25	–	7.32	7.18	7.25	7.72	-60.0
4c	6.42 ^a	5.63	7.81	7.42	7.25	–	7.47 ^b	–	7.36 ^c	7.68 ^d	-60.1

^a broad signal. ^b d, $^4J = 2.1$ Hz. ^c dd, $^3J = 8.5$ Hz, $^4J = 2.1$ Hz. ^d d, $^3J = 8.5$ Hz.

Table 2. ^{13}C -NMR data (δ , ppm; J in Hz; in DMSO- d_6).

comp.	C _A	CF ₃	C of pyrazole							
			C-3		C-4		C-5			
4a	32.8	122.4	138.8	100.4	157.8					
	$^1J = 125.0$	$^1J = 270.0$	$^2J(\text{C3},\text{F}) = 34.5$ $^3J(\text{C3},\text{H}_A) = 4.0$	$^2J(\text{C4},\text{H}_A) = 8.8$	$^3J(\text{C5},\text{H}_A) = 7.9$					
4b	30.9	122.1	137.5	100.2	156.9					
	$^1J = 127.5$	$^1J = 270.1$	$^2J(\text{C3},\text{F}) = 35.4$ $^3J(\text{C3},\text{H}_A) = 4.0$	$^2J(\text{C4},\text{H}_A) = 8.6$	$^3J(\text{C5},\text{H}_A) = 7.3$					
4c	30.7	122.1	137.5	99.8	156.8					
	$^1J = 128.0$	$^1J = 270.1$	$^2J(\text{C3},\text{F}) = 35.7$ $^3J(\text{C3},\text{H}_A) = 4.0$	$^2J(\text{C4},\text{H}_A) = 8.7$	$^3J(\text{C5},\text{H}_A) = 7.0$					
comp.	C of N-phenyl				C of aryl					
	1'	2',6'	3',5'	4'	1''	2''	3''	4''	5''	6''
4a	139.2	120.9	128.6	125.5	143.5	127.0	128.0	125.6	128.0	127.0
4b	138.9	121.1	128.7	125.8	139.7	131.7	129.2	127.7	126.3	130.6
4c	138.8	121.2	128.7	125.9	138.7	132.6	128.6	131.4	126.5	131.9

4,4'-[(2-Chlorophenyl)methylene]bis[1-phenyl-3-(trifluoromethyl)-1H-pyrazol-5-ol] (**4b**)

Under N₂ atmosphere, a mixture of 1-phenyl-3-(trifluoromethyl)-2-pyrazolin-5-one (**1**) (500 mg, 2.19 mmol) and 2-chlorobenzaldehyde (616 mg, 4.38 mmol) was heated at 120-130 °C with stirring for 15 min. After cooling to room temperature, 9 mL of light petroleum and 1 mL of ethyl acetate were added and the mixture was refluxed for 15 min, then allowed to cool slowly to ambient temperature. The precipitated solid was filtered off, washed with the same solvent mixture and dried to afford 453 mg (72 %) of the title compound as colorless crystals, mp 202-204 °C.

IR (KBr) ν (cm⁻¹): 3445 (OH).

MS (EI, 70 eV): (*m/z*, %) M⁺ not found, 350/352 (5/2), 316 (20), 315 (100), 228 (32), 105 (16), 91 (13), 77 (95), 51(29).

Anal. Calcd for C₂₇H₁₇ClF₆N₄O₂ • 1/3 H₂O: C, 55.53%; H, 3.04%; N, 9.58%. Found: C, 55.53%; H, 2.72%; N, 9.50%.

Acknowledgements

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References and Notes

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