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SYNTHESIS OF TRIFLUOROMETHYL, CONTAINING 1-(3,5-DIALKYL-4-HYDROXYBENZYL) -PYRAZOLE AND PYRAZOL-5-ONE DERIVATIVES, AS POTENTIAL FUNGICIDES

AMRENDRA KUMAR SINGH* AND NITIN SINGH SOLUNKEY**

Declaration

The Declaration of the authors for publication of Research Paper in The Indian Journal of Research Anvikshiki ISSN 0973-9777 Bi-monthly International Journal of all Research: We, *Amrendra Kumar Singh and Nitin Singh Solunkey* the authors of the research paper entitled SYNTHESIS OF TRIFLUOROMETHYL, CONTAINING 1-(3,5-DIALKYL-4-HYDROXYBENZYL) -PYRAZOLE AND PYRAZOL-5-ONE DERIVATIVES, AS POTENTIAL FUNGICIDES declare that , We take the responsibility of the content and material of our paper as We ourself have written it and also have read the manuscript of our paper carefully. Also, We hereby give our consent to publish our paper in Anvikshiki journal , This research paper is our original work and no part of it or it's similar version is published or has been sent for publication anywhere else.We authorise the Editorial Board of the Journal to modify and edit the manuscript. We also give our consent to the Editor of Anvikshiki Journal to own the copyright of our research paper.

Abstract

3,5-Dialkyl-4-hydroxybenzylhydrazine(1) reacted with hexafluoroacetylacetone, and trifluoroacetylacetone yielding the pyrazoles (2) bearing trifluoromethyl and/or methyl substituents in positions 3 and 5. The same hydrazine derivatives (1) afforded the pyrazol-5-ones (3) with trifluoroacetoacetic acid ethyl ester. The synthesized compounds have been screened against P.oryzae & H. oryze.

Keywords: fluorination, pyrazole, pyrazolone, trifluoromethyl-1,3-diketones.

Introduction

Fluorine is the most electronegative element and the vander Waals radius of fluorine is close to that of hydrogen, hence the introduction of a fluorine-containing group into an organic molecule brings about some remarkable changes in its physical and chemical properties[1]. Many new fluorinated materials which take advantage of these useful changes, e.g. , drugs and agrochemicals, have been designed[2] and synthesized[3]. Continuing our studies directed toward the synthesis of new fluorine-containing organic compounds in the present paper the reactions of hindered phenol containing hydrazines with hexafluoroacetylacetone, trifluoroacetylacetone and trifluoroacetoacetic acid ethyl ester are reported.

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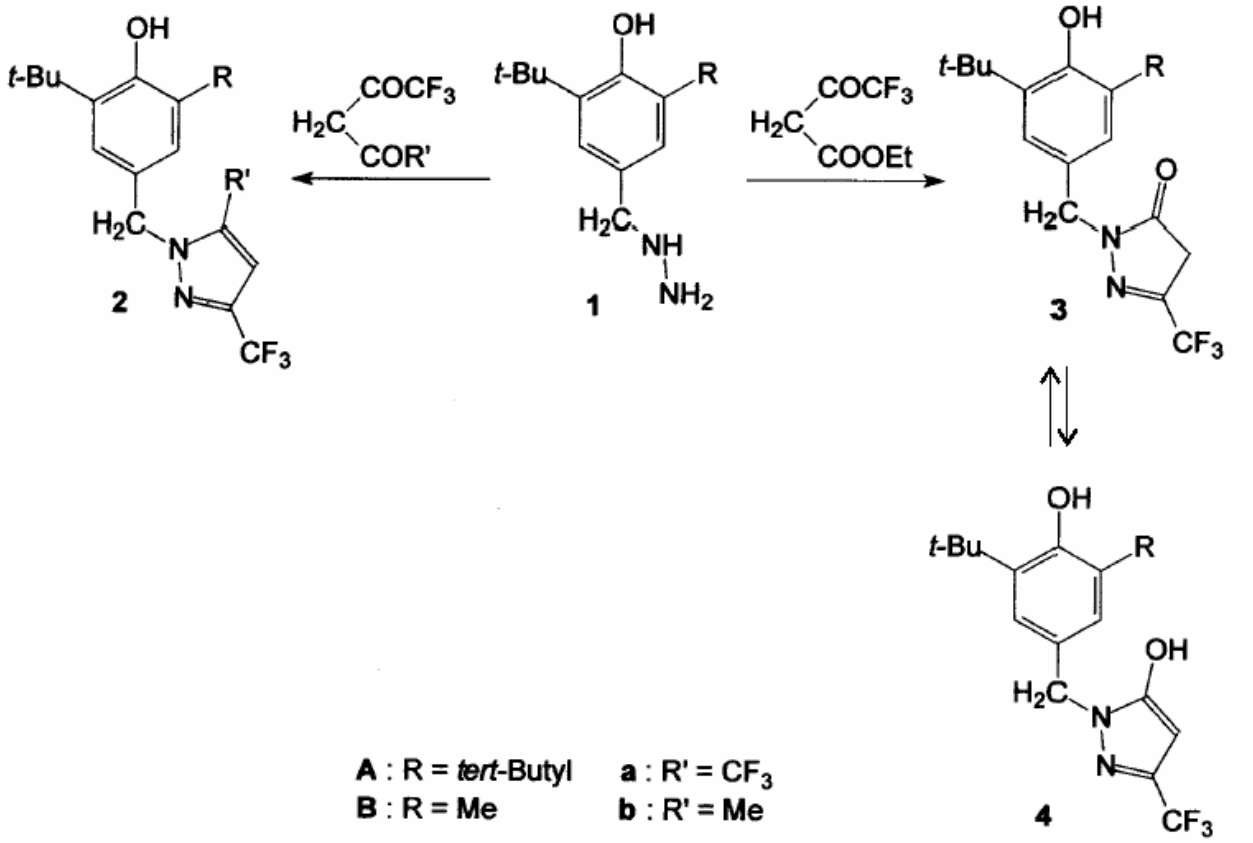
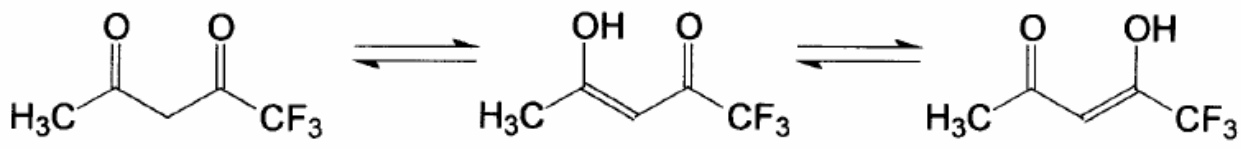
Results and Discussion

3,5-Dialkyl-4-hydroxybenzylhydrazine (1). where the 3,5-dialkyl groups are either both *t* -butyl (series denoted by A)or methyl and t-butyl (series denoted by B), synthesized from hydrazine hydrate and N, N-dimethyl-3,5-dialkyl-4-hydroxybenzylamine according to a literature procedure[8], reacted with hexafluoroacetylacetone, and trifluoroacetylacetone (leading to series denoted by *a* and *b* respectively) yielding the title pyrazole derivatives *2a-b* bearing trifluoromethyl and/or methyl substituents in positions 3 and 5. The same hydrazine derivatives *(1)* afforded, with trifluoroacetoacetic acid ethyl ester, the title pyrazol-5-one derivatives, which might have the tautomeric structures (3) or (4) (Scheme 1); actually, in chloroform solution, only the pyrazolonic (lactamic) tautomer (3) can be detected by ^{1}H-NMR spectrometry.



Scheme 1.

In general, the reaction of monosubstituted hydrazines with unsymmetrical 1,3-diketones can result in the formation of isomeric pyrazoles, depending on the site of initial nucleophilic attack[9]. In the case of trifluoroacetylacetone, enolic species are in equilibrium with the diketone[10,11] (Scheme 2).



Scheme 2.

IR Spectra

The infrared absorption spectra of all the above compounds presented the phenolic O-H stretching band at 3630-3650 cm^{-1} and the aromatic ring vibrations at 1600 and 1485-1500 cm^{-1} . The presence of conjugated C=C and C=N bonds in the pyrazole ring leads to the appearance of two absorption bands at 1500-1600 cm^{-1} . In addition, the pyrazolone derivatives showed C=O stretching bands at 1653 (3A) or 1672 cm^{-1} (3B). Table-1 presents the most characteristic ions in the mass spectra of compounds (2) and (3)

TABLE I. The most characteristic ions in the mass spectra of compounds **2** and **3**

	Ion; *m/z* (relative intensity)				
Comp.	M^+	$(M–CH_3)^+$	$(M–C_5HN_2F_6)^+$	$(M–C_5HN_2F_6O)^+$	$(CF_3)^+$
2Aa	422 (30)	407 (100)	219 (13)	203 (20)	57 (13)
2Bb	380 (35)	365 (100)	177 (20)	161 (67)	57 (5)
Comp.	M^+	$(M–CH_3)^+$	$(M–C_5H_4N_2F_3)^+$	$(M–C_5H_4N_2F_3O)^+$	$(CF_3)^+$
2Ab	368 (53)	353 (100)	219 (13)	203 (45)	57 (8)
2Bb	326 (60)	311 (90)	177 (30)	161 (100)	
Comp.	M^+	$(M–CH_3)^+$	$(M–C_4H_2N_2F_3)^+$	$(M–C_4H_2N_2F_3O)^+$	$(CF_3)^+$
3A	370 (17)	355 (35)	219 (100)	203 (30)	57 (18)
3B	328 (28)	313 (27)	177 (100)	161 (72)	57 (15)

^{1}H-NMR Spectra: The ^{1}H and ^{19}F NMR spectra confirm the structures of all the compounds. The ^{1}H NMR spectrum of (2) displayed the pyrazole H-C (4) as a singlet in the range d6.30-6.87 ppm, indicating that this H is an aromatic pyrazole proton, whereas the ^{1}H NMR spectrum of (3) displayed the H-C (4) as an AB system (doublet at 4.98-5.01 ppm, with the geminal coupling constant J: 18 Hz), indicating that these protons are a prochiral CH_2 group in an asymmetric environment.

Experimental

Melting points reported were determined in open capillary and are uncorrected.The IR spectra were obtained on Perkin-Elmer spectrometer. The ^{1}H- and ^{19}F-NMR spectra were recorded, in $CDCl_3$ as a solvent, on a JEOL Datum (400 MHz) spectrometer. The chemical shifts for the ^{1}H-NMR spectra are reported in dppm downfield from internal TMS, and those for the ^{19}F-NMR spectra are given in d ppm downfield from internal C_6F_6 d ($CFCl_3$) of the C_6F_6 reference being -162.2 ppm. All reactions with air-sensitive compounds were carried out under a nitrogen atmosphere. Column chrornatography was conducted on silica gel. GC analyses were performed using a Hitachi G-5000 instrument (flame ionization detector, FID) with a 30 m column Neutra Bond. Mass spectra were measured on a Hewlett-Packard (HP) 5890 and the El-high-resolution mass spectra were measured on a JEOL JMS-700TZ.

General procedure for the preparation of CF_3 containing pyrazoles and pyrazolones : A mixture of 10 mol 3,5-dialkyl-4-hydroxbenzylhydrazine (1)[4] , and 10 mol CF_3 containing 1,3-diketones in 30 ml ethanol was kept for 30 min at room temperature, then refluxed for l0h (for the syntheses of pyrazoles) and 6h (for the syntheses of pyrazolones). Water was then added and the aqueous layer was extracted with diethyl ether, dried (Na_2SO_4), filtered, concentrated and then purified by flash chromatography on silica gel or by recrystallization.

1-(3,5-Di-t -butyl-4-hydroxybenzyl)-3,5-bis(trifluoromethyl)pyrazole (2Aa). 2Aa was purified by flash chromatography on silica gel, eluting with a 20:1 mixture of hexane and ethyl acetate to give yellow crystals, m.p. 69-70 °C, yield 62 %. ^{1}H-NMR: 1.40 (s, 18H); 5.25 (s, 1H); 5.35 (s, 2H); 6.87 (s, 1H); 7.14 (s, 1H); ^{19}F-NMR: 99.37 (s, 3F); 102.64 (s, 3F); IR (neat, cm^{-1}): 3630-3650 (-OH); MS m / z : 422 ($M^+ + H^+$). HRMS. Calcd. For C_{20} $H_{24}OF_6N_2$ (m/e) : 422. 1792: Found: 410. 1782.

1-(3,5-Di-t -butyl-4-hydroxybenzyl)-5-methyI-3(trifluoromethyl)pyrazole (2Ab). 2Ab was purified by flash chromatography on silica gel. eluting with a 10:1 mixture of hexane and ethyl acetate to give white crystals, m.p. 113-114 °C. yield 62 %. ^{1}H-NMR : 1.39 (s, 18H): 2.26 (s, 3H); 5.20 (s, 1H); 5.22 (s, 2H); 6.30 (s ,1H); 6.95 (s ,1H); ^{19}F-NMR : 99.68 (s, 3F): IR (neat, cm^{-1}): 3630-3650 (OH); MS m/ z : 368 ($M^+ + H^+$). HRMS. Calcd. For $C_{20}H_{27}OF_3N_2$ (m/e): 368.2075; Found: 358.2074.

1 -(3-t -Butyl-4-hydroxy-5-methylbenzyl)-3,5-bis (trifluoromethyl) pyrazole (2Ba). 2Ba was purified by recrystallizations fron n -heptane, white crystals, m.p. 68 °C, yield 54 %. ^{1}H-NMR : 1.38 (s, 9H); 2.22 (s, 3H); 4.80 (s, 1H); 5.34 (s, 2H); 6.87 (s, 1H); 6.95 (s, 1H):7.10 (d,J=1.70Hz,lH); ^{19}F-NMR: 99.44 (s, 3F); 102.57 (s, 3F); IR (neat, cm^{-1}) : 3630 3650 (OH): MS m/z : 380 ($M^+ + H^+$). HRMS. Calcd. For $C_{17}H_{18}OF_6N_2$ (m/e): 380,1336: Found: 378.1321.

1-(3-t) -Butyl-4-hydroxy-5-methylbenzyl)-5-methyl-3-(trifluoromethyl)pyrazole (2 Bb): 2Bb was purified by recrystallizations from n -heptane, white crystals, m.p. 112-14 °C. yield 63 %. ^{1}H-NMR: 1.36 (s, 9H); 2.19 (s, 3H); 2.23 (s, 3H); 4.77 (s, 1H); 5.20 (s, 2H); 6.30 (s, 1H); 6.76 (s, 1H); 6.94 (d, J = 1.70Hz, 1H); ^{19}F-NMR: 99.78 (s, 3F); IR (neat, cm^{-1}): 3630-3650 (OH); MS m/z : 326 ($M^+ + H^+$). HRMS. Calcd. for $C_{17}H_{21}OF_3N_2$ (rn/e) : 326.1606; Found: 316.1824.

1-(3,5-Di-t -butyl-4-hydroxybenzyl)-3-(trifluoromethyl) pyrazol-5-one (3 A). 3A was purified by recrystallizations from n-heptane, white crystals, m.p. 218-220 °C, yield 64 %. ^{1}H-NMR: 1.38 (s, 18H); 3.27 (s, 2H); 5.01 (d,J = 18 Hz, 2H); 5.72 (s, 1H); 6.95 (s, 1H); ^{19}F-NMR: 101.17 (s, 3F); IR (neat, cm^{-1}): 3630-3650 (OH); 1653 (C=O); MS m/z : 370 ($M^+ + H^+$). HRMS. Calcd. For $C_{19}H_{25}OF_3N_2$ (m/e) : 370.1866; Found: 368.1864.

1-(3-t -Butyl-4-hydroxy-5-methylbenzyl)-3-(trifluoromethyl)pyrazol-5-one (3). 3B was purified by recrystallizations from n-heptane, white crystals, m.p. 180-190 °C, yield 60 %. ^{1}H-NMR: 1.38 (s, 9H); 2.14 (s, 3H); 3.30 (5, 2H); 4.98 (d, J- 18 Hz, 2H); 5.73 (s, 1H); 6.83 (s, 1H); 6.93 (d, J= 1.70 Hz, 1H); ^{19}F-NMR: 101.24 (s, 3F); IR (neat, cm^{-1}): 3630-3650 (OH); 1672 (C=O); MS m/z : 328 ($M^+ + H^+$). HRMS. Calcd. for $C_{16}H_{19}OF_3N_2$ (m/e) : 326.1384; Found: 328.1383.

Antifungal Activity

All compounds were evaluated for their anti-fungal activity against fungies P. Oryzae, H. Oryzae at 3 concentrations VIZ : 10 ppm, 100 ppm & 1000 ppm by employing food poisoning of solidified agar technique[13]. The average (of three replication) % inhibited after 96 hours determined and result were compared with thos abtained using the commercial fungicide Orthophaltan (wp 50%) It is evident from result that all compounds are toxic against fungus P. Oryzae and H. oryzae, but lower concentration the observed fungitoxicities were considerable lower than those observed with Orthophaltan.

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