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# Reactions of 4-Benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic Acid with Hydrazides

DILEK ÜNAL* and BEHZAT ALTURAL
*Department of Chemistry, Erciyes University, 38039 Kayseri, Turkey*
*Fax: (90)(352)4374933; E-mail: dilekunal@gmail.com*

The reaction of substituted pyrazole ring **3** with various hydrazides (**4a-f**) furnished the corresponding pyrazole carbohydrazides (**5a-f**). The structures of the novel compounds were confirmed by elemental analysis, IR, $^{1}H$ and $^{13}C$ NMR spectroscopic measurements.

**Key Words: 2,3-Furandione, 1*H*-Pyrazole-3-carboxylic acid, Hydrazide.**

## INTRODUCTION

4-Acyl-5-alkyl/aryl-2,3-dihydro-2,3-furandiones are obtained from the starting materials, 1,3-dicarbonyl compounds and oxalyl chlorides[1]. The formation of 4-benzoyl-5-phenyl-1,3-furandione (**1**)[1] and 4-benzoyl-1,5-diphenyl-1*H*-pyrazole-3-carboxylic acid (**2**)[2] have been reported recently. The reactions of **1** and the corresponding 1*H*-pyrazole carboxylic acid chloride (**3**) synthesized from the reaction of **2** and thionyl chloride, with various nucleophiles and hydrazines have been recently reported in different solvents and conditions[3-6].

The derivatives of pyrazole and their chemistry have found considerable attention during the decades due to outstanding biological activities such as antimicrobial[7], antitumor[8], antiviral[9] and antihistaminic[10] activities, as well as to interesting properties in commercially important dyestuffs[11].

Here, in this paper, we have extended our investigations into the reactions of **3** with various acyl hydrazines, hydrazides, **4a-f** namely.

## EXPERIMENTAL

All solvents were dried by refluxing with the appropriate drying agent and distilled before use. All melting points were determined by the use of Büchi melting point apparatus and not corrected. Microanalyses were performed on a Carlo-Erba Elemental Analyzer Model 1108. The IR spectra of the compounds were obtained by Shimadzu FTIR 8400. $^{1}H$ and $^{13}C$ NMR spectra of them were obtained from Bruker 400 MHz ($\delta$ in ppm). All experiments were followed by TLC using DC Alufolien Kieselgel 60F 254 Merck and with a Camag TLC Lamp (254/366 nm).

**N',1,4,5-Tetraphenyl-1*H*-pyrazole-3-carbohydrazide (5a):** 0.39 g of **3** was dissolved in 20 mL of benzene. To this solution, 0.14 g of benzoic hydrazide (**4a**) dissolved in benzene was added dropwise and the reaction mixture was refluxed during 2 h. Evaporation of the solvent gives the crude **5a** which is recrystallized by 1:1 ether-petroleum ether mixture to yield 0.41 g (85 %); $C_{30}H_{22}N_4O_3$, 486.52 g/mol, m.p. 132 ºC; IR ($\nu_{max}$, $cm^{-1}$): 3300-3000 (-NH-NH-); 1661 (C=O); $^1$H NMR ($CDCl_3$, δ): 9.95 and 9.34 (d, -NH-NH-), 7.82-7.05 ppm (m, 23H, aromatic H); $^{13}$C NMR ($CDCl_3$, δ): 191.55 ppm (C=O, benzoyl), 164.16 and 157.62 (C=O, hydrazides); Elemental analysis (%): Found (Calcd.) C: 74.19 (74.06); H: 4.42 (4.56); N: 11.52 (11.53).

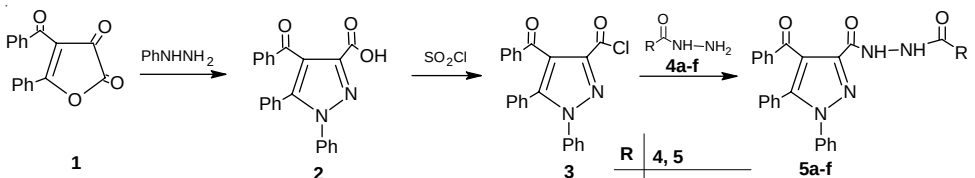
**4-Benzoyl-1,5-diphenyl-N'-[(4-nitrophenyl)carbonyl]-1*H*-pyrazole-3-carbohydrazide (5b):** 0.39 g of **3** was dissolved in 20 mL of benzene. To this solution, 0.18 g of 4-nitro benzoic hydrazide (**4b**) dissolved in benzene was added dropwise and the reaction mixture was refluxed during 1 h. Evaporation of the solvent gives the crude **5b** which is recrystallized by 1:1 ether-petroleum ether mixture to yield 0.43 g (80 %); $C_{30}H_{21}N_5O_5$, 531.52 g/mol, m.p. 149 ºC; IR ($\nu_{max}$, $cm^{-1}$): 3209-3033 (-NH-NH-); 1699, 1677, 1635, 1654 (C=O); $^1$H NMR ($CDCl_3$, δ): 9.81 and 9.24 (d, -NH-NH-), 7.99-7.00 ppm (m, 22H, aromatic H); $^{13}$C NMR ($CDCl_3$, δ): 191.27 (C=O, benzoyl), 164.42 and 160.03 (C=O, hydrazides), 149.78-122.51 (aromatic C); Elemental analysis (%): Found (Calcd.) C: 67.42 (67.79); H: 3.77 (3.98); N: 13.12 (13.18).

**4-Benzoyl-1,5-diphenyl-N'-(phenylacetyl)-1*H*-pyrazole-3-carbohydrazide (5c):** 0.39 g of **3** was dissolved in 20 mL of benzene. To this solution, 0.15 g of phenyl acetyl hydrazide (**4c**) dissolved in toluene was added dropwise and the reaction mixture was refluxed during 2 h. Evaporation of the solvent gives the crude **5c** which is recrystallized by 1:1 ether-petroleum ether mixture to yield.0.43 g (86 %); $C_{31}H_{24}N_4O_3$, 500.55 g/mol, m.p. 174 ºC; IR ($\nu_{max}$, $cm^{-1}$): 3359-3247 (-NH-NH-); 1707, 1679, 1661 (C=O); $^1$H NMR ($CDCl_3$, δ): 9.66 and 9.68 (d, -NH-NH-), 7.02-7.85 (m, 23H, aromatic H), 3.47 ppm (s, 1H, $-CH_2-$); $^{13}$C NMR ($CDCl_3$, δ): 191.37 (C=O, benzoyl), 167.96 and 157.57 (C=O, hydrazides), 122.04-144.15 (aromatic C), 40.99 ppm ($-CH_2-$); Elemental analysis (%): Found (Calcd.) C: 74.36 (74.38); H: 4.48 (4.83); N: 11.19 (11.19).

**4-Benzoyl-1,5-diphenyl-N'-[(2-nitrophenyl)carbonyl]-1*H*-pyrazole-3-carbohydrazide (5d):** 0.39 g of **3** was dissolved in 20 mL of benzene. To this solution, 0.18 g of 2-nitro benzoic hydrazide (**4d**) dissolved in benzene was added dropwise and the reaction mixture was refluxed during 2 h. Evaporation of the solvent gives the crude **5d** which is recrystallized by 1:1 ether-petroleum ether mixture to yield 0.4 g (75 %); $C_{30}H_{21}N_5O_5$, 531.52 g/mol, m.p. 140 ºC; IR ($\nu_{max}$, $cm^{-1}$): 3232-3184 (-NH-NH-); 1666, 1639, 1660 (C=O); $^1$H NMR ($CDCl_3$, δ): 10.21 and 9.86 (d, -NH-NH-), 7.11-7.92 (m, 22H, aromatic H); 191.37 (C=O, benzoyl), 170.89 and 162.69 (C=O, hydrazides), 158.69-122.14 (aromatic C); Elemental analysis (%): Found (Calcd.) C: 68.08 (67.79); H: 3.85 (3.98); N: 13.18 (13.18).

**N'-Acetyl-4-benzoyl-1,5-phenyl-1*H*-pyrazole-3-carbohydrazide (5e):** 0.39 g of **3** was dissolved in 20 mL of benzene. To this solution, 0.07 g of acetic hydrazide (**4e**) dissolved in benzene was added dropwise and the reaction mixture was refluxed during 2 h. Evaporation of the solvent gives the crude **5e** which is recrystallized by 1:1 ether-petroleum ether mixture to yield.0.37g (86 %); $C_{25}H_{20}N_4O_3$, 424.45 g/mol, m.p. 118 ºC; IR ($\nu_{max}$, $cm^{-1}$): 3232-3057 (-NH-NH-); 1662 (C=O); $^1$H NMR ($CDCl_3$, δ): 9.66 and 9.07 (d, -NH-NH-), 7.81-7.13 (m, 15H, aromatic H), 1.93 ppm (s, 3H, $-CH_3$); Elemental analysis (%): Found (Calcd.) C: 70.84 (70.74); H: 4.73 (4.75); N: 13.25 (13.20).

**4-Benzoyl-1,5-diphenyl-N'-(cyanoacetyl)-1H-pyrazole-3-carbohydrazide (5f):** 0.39 g of **3** was dissolved in 20 mL of xylene. To this solution, 0.10 g of cyano acetic hydrazide (**4f**) dissolved in xylene was added dropwise and the reaction mixture was refluxed during 2 h. Evaporation of the solvent gives the crude **5f** which is recrystallized by 1:1 ether-petroleum ether mixture to yield. 0.36.g (80 %); $C_{26}H_{19}N_5O_3$, 449.46 g/mol, m.p.: 124 ºC; IR ($\nu_{max}$, $cm^{-1}$): 3259-3064 (-NH-NH-); 1666 (C=O); $^1$H NMR ($CDCl_3$, δ): 10.00 and 10.14 (d, -NH-NH-), 7.85-7.07 (m, 15H, aromatic H); 3.32 ppm ($-CH_2-$); $^{13}$C NMR ($CDCl_3$, δ): 191.62 (C=O, benzoyl), 159.38 and 157.97 (C=O, hydrazides), 144.66-121.76 (aromatic C), 113.68 (-C≡N), 23.86 ppm ($-CH_2-$); Elemental analysis (%): Found (Calcd.) C: 69.70 (69.48); H: 4.27 (4.26); N: 15.23 (15.58).




| R | 4, 5 |
|---|---|
| a | -Ph |
| b | -Ph-$NO_2$(p) |
| c | -$CH_2$-Ph |
| d | -Ph-$NO_2$(o) |
| e | -$CH_3$ |
| f | -$CH_2$-CN |

**Scheme-I**

## RESULTS AND DISCUSSION

In present study, the reaction of pyrazole nucleus (**3**) with acyl hydrazines namely hydrazides has been investigated. The preparation of substituted pyrazole hydrazides (**4a-f**) were achieved by refluxing equimolar amounts of the pyrazole (**3**) and hydrazides in dry benzene, toluene or xylene for 1-2 h. (**Scheme-I**). These products of the reactions were easily obtained in moderate yields (80-86 %) from nucleophilic addition of **4a-f** to **3** (**Scheme-I**).

The structures of the compounds were confirmed by their elemental analysis, IR, $^{1}$H NMR and $^{13}$C NMR spectroscopic data. The formation of **5a** is supported by the results of spectroscopic measurements in presence of 3 carbonyl peaks in $^{13}$C NMR at 157.62, 164.16 and 191.55 ppm.

Similarly, the spectroscopic data of **5f** proves the structural confirmation. The peaks observed in the $^{13}$C NMR spectrum of the compound at 157.97, 159.38, 191.62 ppm belongs to the three carbonyl groups, two from hydrazides, whereas the 113.68 ppm peak belongs to the cyano group C atom in the structure.

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## REFERENCES

1. (a) E. Ziegler, M. Eder, C. Belegratis and E. Prewedourakis, *Monatsch. Chem.*, **98**, 2249 (1967); (b) E. Ziegler, G. Kollenz and H. Igel, *Monatsch. Chem.*, **102**, 1769 (1971); (c) G. Kollenz, C.O. Kappe and H.A. E-Nabe, *Heterocycles*, **32**, 669 (1991); (d) R.W. Saalfrank, T. Lutz, B. Hörner, J. Gündel, K. Peters and H.G. von Schnering, *Chem. Ber.*, **124**, 2289 (1991).
2. Y. Akçamur, A. Sener, A. M. Ipekoglu and G. Kollenz, *J. Heterocycl. Chem.*, **34**, 22 (1997).
3. (a) A. Sener, R. Kasimogullari, M.K. Sener, I. Bildirici and Y. Akçamur, *J. Heterocycl. Chem.*, **39**, 869 (2002) ; (b) M. Dinçer, N. Özdemir, I. Yildirim, E. Demir, Y. Akçamur and S. Isik, *Acta Cryst.*, **E60**, 317 (2004); (c) I.Ö. Ilhan, Y. Akçamur, E. Saripinar and E. Aslan, *Asian J. Chem.*, **l5**, 1373 (2003).
4. C. Arici, D. Ülkü, M. Saçmaci, S.H. Üngören and Y. Akçamur, *Acta Cryst.*, **E60**, 865 (2004).
5. E. Akbas, I. Berber, A. Sener and B. Hasanov, *IL Farmaco*, **60**, 23 (2005).
6. A. Sener and I. Bildirici, *Turk. J. Chem.*, **28**, 149 (2004).
7. R. Sridhar, P.T. Perumal, S.Etti, G. Shanmugam, M.N. Ponnuswamy, V.R. Prabavathy and N. Mathivanan, *Bioorg. Med. Chem. Lett.*, **14**, 6035 (2004).
8. S.A.F. Rostom, M.A. Shalaby and M.A. El-Demellawy, *Eur. J. Med. Chem.*, **38**, 959 (2003).
9. S.L. Janus, A.Z. Magdif, B.P. Erik and N. Claus, *Monatsh. Chem.*, **130**, 1167 (1999).
10. P.D. Mishra, S. Wahidullah and S.Y. Kamat, *Indian J. Chem. Soc.*, **37B**, 199 (1998).
11. H.Z. Shams, M.H. Helal, F.A.Mohamed and S.A. Abd-Elhafiz, *Pigment Resin Tech.*, **30**, 158 (2001).

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