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One-Pot Synthesis of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one from o-phthalaldehydic acid and 2,4-dinitrophenylhydrazine

Dr.abdul hakim R.Beetru
Chemistry Department, Faculty of Education, Zawia University, Libya.

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Abstract: An efficient and facile method for the synthesis of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one in a single step and very good yield (86%) by condensation of *o*-phthalaldehydic acid and 2,4-dinitrophenylhydrazine using a polar solvent (methanol) at room temperature, The reaction occurred selectivity at carbon no.3 of the lactol form of the *o*-phthalaldehydic acid acid. None of the Schiff bases of type (**B**) and cyclic product of type (**C**) have been formed. The structure of the product was confirmed from their spectral data (^{1}H-NMR, ^{13}C-NMR, and IR) and analytical data.

Key words: syntheses, o-phthalaldehydic acid, condensation, phthalide.

Introduction

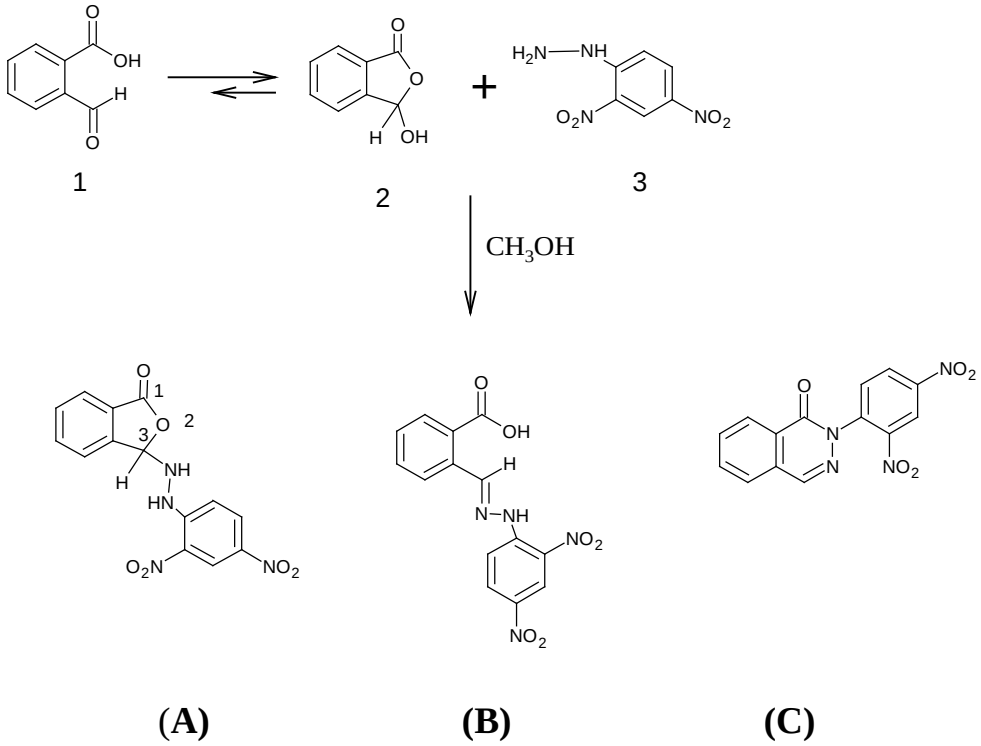
It is well known that 2-formylbenzoic acid (**1)** exist in tautomeric structure both open and closed forms. Amer and Racine[1,2] reported that in aqueous solutions 3-hydroxyphthalide (**2)** closed form exists in about (93%) scheme-1. The reaction of (**1**) with aniline and its derivatives and with 3-aminoquinoline have been explained[3,4] to occur through (S_N2) nucleophilic substitution reactions affording N-(3-phthalidy)amines. Others[5,6,7] shows that some aromatic amines afforded Schiff bases (**B**) and cyclic products of type (**C**). The interesting biological activity that a variety of N-(3-phthalidy)amines shows[8-15] as a herbicide, fungicide, germicide, pesticidal, hypotensive and vasorelaxant activities. In addition, phthalide is a versatile synthetic building block, particularly for the synthesis of carbocyclic and heterocyclic compounds. As part of our ongoing research on 3-substituted phthalides we decided to study the reaction of o-phthalaldehydic acid (**1**) with hydrazine derivatives (**3**) 2,4-dinitrophenylhydrazine in very mild condition.

Results and Discussion

As extension to our work the reaction of *o*-phthalaldehydic acid (**1**) with aryllhydrazine derivatives was studied. The reaction of *o*-phthalaldehydic acid (**1**) with 2,4-dinitrophenylhydrazine (**3**) in stirring methanol at room temperature afforded a crystallisable solid product. The analytical data of isolated phthalide given in table-1. TLC of the crude product indicating the presence of one single component. 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one(**A**).

The IR (KBr) spectrum Table 3 and Fig.3 of the isolated compound shows clearly absorption at 1737 cm^{-1} indicating the presence of the lactonic group, and absorption at 3335 cm^{-1} due to (N-H) stretching and two absorptions bands at 1306 cm^{-1} and 1450 cm^{-1} for two nitro groups (NO_2). On the other hand, The ^{1}H-NMR (d_6-DMSO) spectrum, Fig. **1** and table **2** shows one proton as a broad singlet at δ 6.80, due to phthalidyl proton CH-N, H-3, the deshielding of H-3 in this compound, compared with CH-N-alkyl analogs can be attributed to the anisotropic effect caused by hetero-aromatic ring Table-2, seven protons multiplet at δ 6.97-8.03 due to seven aromatic protons, one proton doublet at δ 8.34 assigned to N-H, one proton broad singlet at δ 8.56 assigned to (NH). Furthermore, ^{13}C -NMR(d_6-DMSO) spectrum Fig.**2** showed seventeen resolved carbon signals, the carbonyl carbon signal was observed at δ 158. The aniline carbon (C-NH) signal was observed at δ142.44 the rest of the resolved carbon signals are corresponding to the aromatic carbon atoms of the product these results clearly indicate the formation of N-(3-phthalidyl)amine of type (**A**) (3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one). The reaction occurred selectivity at carbon no.3 of the lactol form of the *o*-phthalaldehydic acid, and the product resulted from the (S_N2) nucleophilic substitution reaction at carbon no.3 and the leaving group is H_2O. . No absorption band due to stretch (OH) in carboxylic acid group appearing in the region 3000-2400 cm^{-1} and no absorption band due to stretch (C=N) appearing in the region 1630 cm^{-1} these data rules out the presence of the Schiff's base of type (**B**). And no absorption band due to stretch (C=O, N-CO) amide group appearing in the region 1670 cm^{-1} these results rule out the possibility of cyclic product formation of type (**C**).

Scheme-1



Experimental

All melting points were measured on electrotherrmal melting point and were uncorrected, Fourier Transform IR spectrometer, model IFS 25 FTIR, ^{13}C- and ^{1}H-NMR were measured using a Bruker operating at 400 MHz spectrometer. Reagents and solvent for synthesis were obtained from Alderich Chemical Co., and were used without additional purification.

Reaction of *o*-phthalaldehydic acid (1) with 2,4-dinitrophenylhydrazine (3) (General method)

(1.5 g ., 0.01 mole) of *o*-phthalaldehydic acid and (1.98 g ., 0.01 mole) of 2,4-dinitrophenylhydrazine in (15ml) methanol was stirred at room temperature. The mixture was cooled, and the separated solid product were collected and recrystallization the product using n-Propanol.

Table-1
Analytical data of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one.

Phthalide	Molecular Formula	Yield (%)	Color	Melting point (C^0)	Solvent for Crystallization
3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one	$C_{14}H_{10}N_4O_6$	87	Orange	254-256	n-Prppanol

Table-2
Spectral data (C^{13} and ^{1}H-NMR) of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one in DMSO.

Phthalide	^{13}C- NMR (DMSO-d_6,TMS, ppm)	^{1}H-NMR (DMSO-d_6,TMS, ppm)
3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one.	114.94,124.52,125.08, 126.41,126.69,127.42,127.76,128. 25,128.25.129.50, 129.77,130,08,132.77,134.35,139. 15,142.44,158.80.	6.80(br,s,H-3), 6.97-8.03 (m,7H, aromatic protons), 8.34(d, 1H,NH), 8.56(br,s,1H,NH).

Table-3
Spectral data (IR) of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one.

Phthalide	IR (KBr, cm-1)
3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one.	3335 (NH), 1737(C = O), 1658(C = C),1306 (NO_2)and 1450(NO_2),1306 (C-N),1450 Scissor(NH),686(=CH) Aromatic oop,

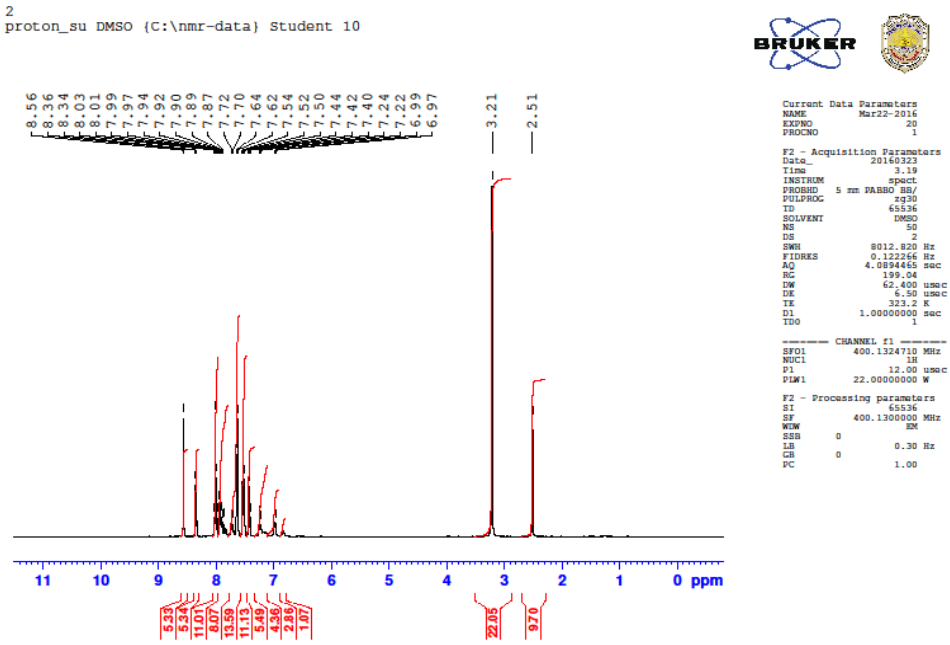


Fig.1.[1]H-NMR spectrum of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one in DMSO .

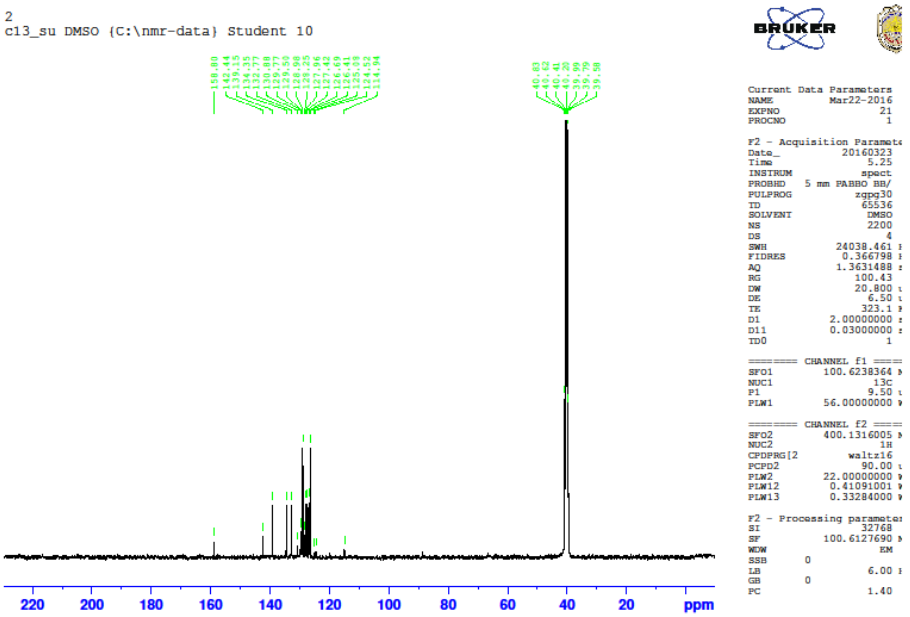


Fig.2.^{13}C -NMR spectrum of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one in DMSO.

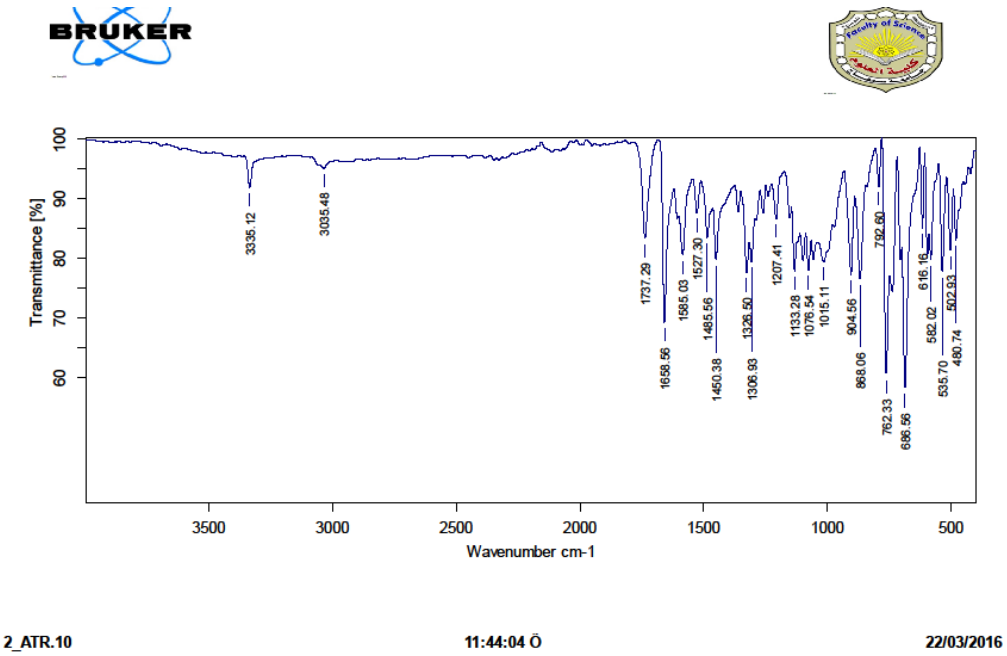


Fig.3. IR of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one.

References

[1]. Amer, A,; Zimmer, H. J. Heterocyclic Chem. 1981, 18, 1625.

[2]. Racine,S. Ber. 1886. 19,778.

[3]. A. R. Betrow,; K. M. Hamza and R. M. Tarhouni. Zawia University, Bulletin, Number (15 – vol. 3), 2013.

[4]. A. R. Betrow,; K. M. Hamza,; k.T. Elozi and E.O.Elakeshe. Zawia University, Bulletin, Number (16 –vol. 3)July,(5-12) 2014.

[5]. Mario and Gbelordoni, Ann, Chim.(Rome), 64, 421, 1974.

[6]. Sherine. N. Khattab,; Seham. Y. Hassan., Journal of Heterocyclic Chemistry, September , vol.44 (617-626) 2007.

[7]. Castle, R. N,; Takano, S. Journal of Heterocyclic Chemistry, 1966, 3, 381.

[8]. 8 - K. B. Sloan, S. M. Koch, J. Org. Chem , 48, 635 , (1983).

[9]. 9 - Ogawa, Yoshimitu, Chin. J P. 6383, 13 Apc. (1988), C. A. 109. 128818 J. (1988).

[10]. 10 - D. D. Wheeler, D .C. Yong; to Do Chemical Co. U, 756, Chem, Abst 56, 1399, (1962)

[11]. 11- Aoki, K., furusho, T., Kimura, T., Satake, K. & Funayama, S. (1973). Jpn Patent No. 7 324 724

[12]. 12- Aoki, K., Furusho, T., Kimura, T., Satake, K. & Funayama, S. (1974). Chem. Abstr.80, 129246.

[13]. 13- Bellasio, E. (1974). German Patent No. 2 422 193

[14]. 14- Bellasio, E. (1975). Chem. Abstr. 83, 9788

[15]. 15- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995).