

تصنيع مركب 3- [2, 4- ثنائي نيتروفنيل هيدرازيل] -2-
بنزوفوران-1-
- اون من تكاثف حمض اورثو- فثالالديهيدريك مع 4,2- ثنائي
هيدرازي (H3) نيتروفنيل

د. عبد الحكيم رحومه بيترو ، د. خالد الطاهر العوزي ، د. خيري محمد حمزة
د. محمد المبروك زريق
كلية التربية- جامعة الزاوية - كلية العلوم - جامعة الزاوية

ملخص البحث

نظراً لما تتمتع به مشتقات الفثاليدات من أهمية حيوية ؛ لذلك تمت في هذا الورقة البحثية تحضير مركب (-2-[2-(2,4-dinitrophenyl)hydrazinyl]-3-benzofuran-1(3H)-one) من خلال تكاثف حمض أورثو- فثالالديهيدريك مع مشتق الهيدرازين (4,2 - ثنائي نيترو فنيل هيدرازين) واستخدام الميثانول كمذيب والتفاعل تم في خطوة واحدة عند درجة حرارة الغرفة، وبمردود عالي (86%) والتفاعل حدث على ذرة الكربون رقم- 3 لشكل اللاكتون (المغلق) للحامض. لم تتكون قواعد شيف من نوع (B) ولا ناتج حلقي من نوع (C). تم تشخيص الناتج باستخدام الأجهزة الطيفية مثل طيف الأشعة تحت الحمراء (IR) وأطياف الرنين النووي المغناطيسي (^1H and ^{13}C -NMR).

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

Abstract:

An efficient and facile method for the synthesis of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3H)-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. 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 ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and IR) and analytical data.

Key words: one-pot synthesis, *o*-phthalaldehydic acid, phthalides.

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_{N}^2) nucleophilic substitution reactions affording N-(3-phthalidy)amines. Others^{5,6,7} show 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 to 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.

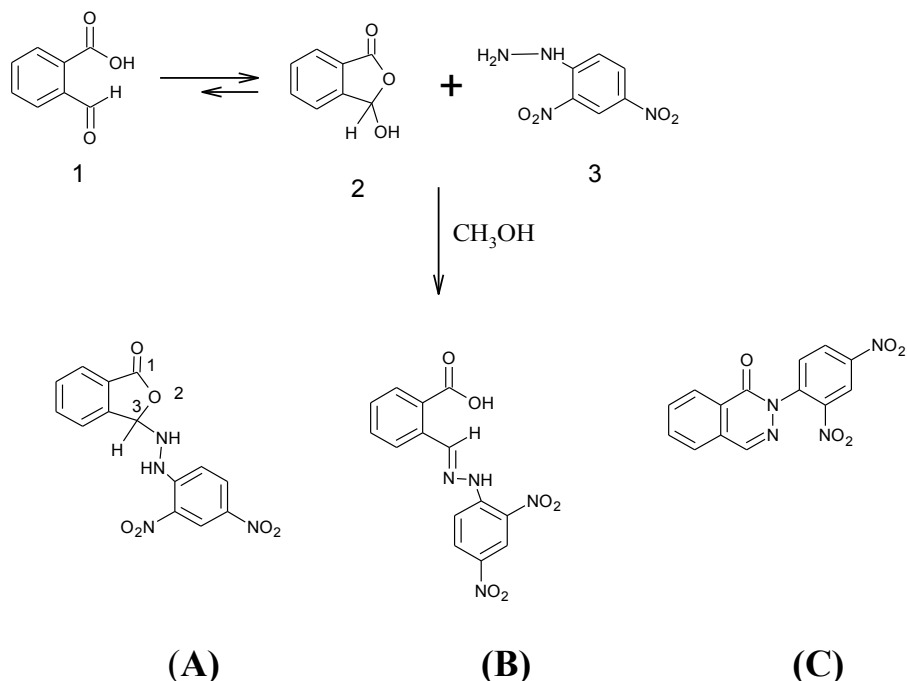
RESULTS AND DISCUSSION:

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 is 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 $^1\text{H-NMR}$ ($\text{d}_6\text{-DMSO}$) spectrum, Fig. 1 and table 2 show one proton as a broad singlet at $\delta\ 6.80$, 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 $\delta\ 6.97\text{-}8.03$ due to seven aromatic protons, one proton doublet at $\delta\ 8.34$ assigned to N-H, one proton broad singlet at $\delta\ 8.56$ assigned to (NH). Furthermore, ^{13}C -NMR($\text{d}_6\text{-DMSO}$) spectrum Fig.2 showed seventeen resolved carbon signals, the carbonyl carbon signal was observed at $\delta\ 158$. The aniline carbon (C-NH) signal was observed at $\delta\ 142.44$ 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_N^2) 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 $3000\text{-}2400\text{ cm}^{-1}$ 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 electrothermal melting point and were uncorrected, Fourier Transform IR spectrometer, model IFS 25 FTIR, ¹³C- and ¹H-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

تصنيع مركب 3-[2-(2,4-ثنائي نيتروفينيل هيدرازينيل)]-2-بنزوفوران-1-
 د.عبد الحكيم رحومه بيثرو د.خالد الطاهر العوزي د.خيري محمد حمزة
 د.محمد المبروك زريق

was stirred at room temperature. The mixture was cooled, and the separated solid product was 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 <i>H</i>)-one	C ₁₄ H ₁₀ N ₄ O ₆	87	Orange	254-256	n-Prppanol

Table-2
Spectral data (C¹³ and ¹H-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 <i>H</i>)-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).

تصنيع مركب 3-[2-(2,4-ثنائي نيتروفينيل هيدرازينيل)]-2-بنزوفوران-1-1-
 د.عبد الحكيم رحومه بيثرو د.خالد الطاهر العوزي د.خيرى محمد حمزة
 د.محمد المبروك زريق

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

Phthalide	IR (KBr, cm-1)
3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3H)-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,

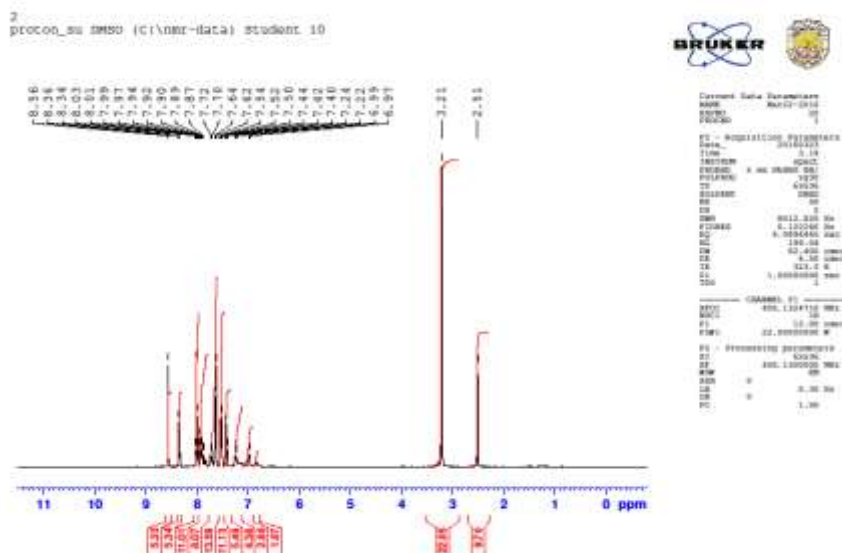


Fig.1. ¹H-NMR spectrum of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3H)-one in DMSO .

تصنيع مركب 3-[2-(2,4-ثنائي نيتروفينيل هيدرازينيل)]-2-بنزوفوران-1-*D*.
 د.عبد الحكيم رحومه بيثرو د.خالد الطاهر العوزي د.خيربي محمد حمزة
 د.محمد المبروك زريق

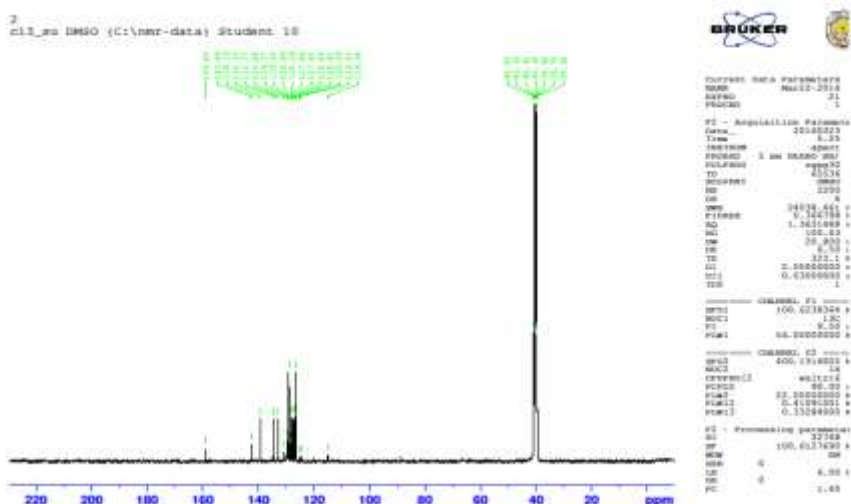


Fig.2. ^{13}C -NMR spectrum of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one in DMSO.

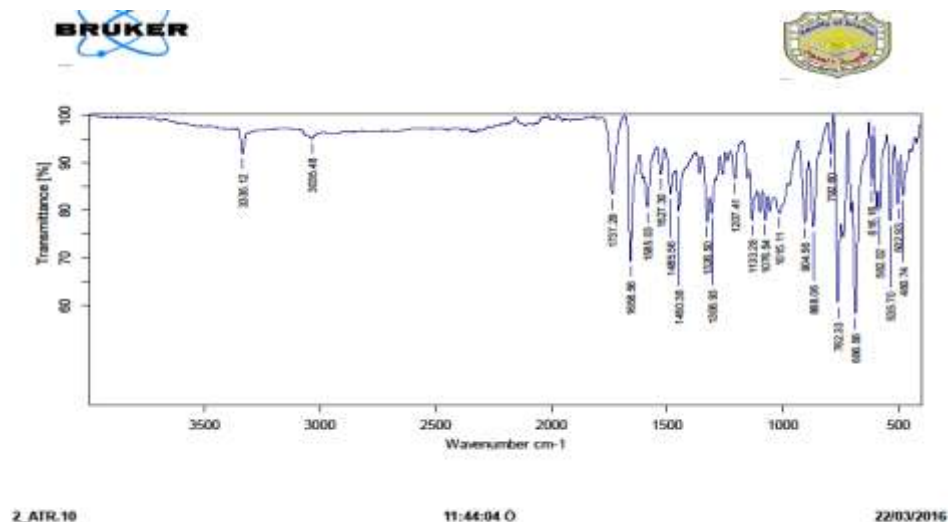


Fig.3. IR of 3-[2-(2,4-dinitrophenyl)hydrazinyl]-2-benzofuran-1(3*H*)-one.

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 - K. B. Sloan, S. M. Koch, J. Org. Chem , 48, 635 , (1983).
- 9 - Ogawa, Yoshimitu, Chin. J P. 6383, 13 Apc. (1988), C. A. 109. 128818 J. (1988).
- 10 - D. D. Wheeler, D .C. Yong; to Do Chemical Co. U, 756, Chem, Abst 56, 1399, (1962)
- 11- Aoki, K., furusho, T., Kimura, T., Satake, K. & Funayama, S. (1973). Jpn Patent No. 7 324 724
- 12- Aoki, K., Furusho, T., Kimura, T., Satake, K. & Funayama, S. (1974). Chem. Abstr. 80, 129246.
- 13- Bellasio, E. (1974). German Patent No. 2 422 193
- 14- Bellasio, E. (1975). Chem. Abstr. 83, 9788
- 15- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995).