Synthesis of some new 1-aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles using the Vilsmeier–Haack reaction — Isolation of the key intermediate 1-aryl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles

Ajay Kumar, Om Prakash, Mayank Kinger, and Shiv P. Singh

Abstract: Arylhydrazones of dehydroacetic acid (DHA) underwent Vilsmeier–Haack reaction to generate the corresponding 1-aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**1**) with the pyrone moiety of the DHA remaining intact. However, when the reaction was performed using 1 equiv. of the reagent, compounds of 1-aryl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**2a**–**2f**) were obtained, which underwent smooth conversion to 1-aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**1**) on further treatment with another equivalent of the Vilsmeier–Haack reagent. This unreported observation suggests the intermediacy of 1-aryl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**2**) in Vilsmeier–Haack reactions of hydrazones with a pyrone moiety. Several analogous compounds were also prepared using arylhydrazones of DHA.

Key words: dehydroacetic acid, pyrazoles, Vilsmeier–Haack reaction, 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one.

Résumé : Les arylhydrazones de l'acide déhydroacétique (DHA) subissent la réaction de Vilsmeier–Haack pour conduire à la formation des 1-aryl-4-formyl-3-(4-hydroxy-6-méthyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**1**) dans lesquelles la portion pyrone de l'acide DHA demeure intacte. Toutefois, lorsque la réaction est effectuée en utilisant un équivalent de réactif, on obtient plutôt les 1-aryl-3-(4-hydroxy-6-méthyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**2a**–**2f**) qui, sous l'influence d'un autre équivalent de réactif de Vilsmeier–Haack, se transforment facilement en 1-aryl-4-formyl-3-(4-hydroxy-6-méthyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**1**). Cette observation qui n'avait jamais été rapportée antérieurement suggère que les 1-aryl-3-(4-hydroxy-6-méthyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**2**) sont des intermédiaires dans les réactions de Vilsmeier-Haack comportant une portion pyrone. On a préparé plusieurs composés analogues à partir d'autres arylhydrazones de l'acide DHA.

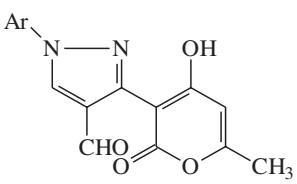
Mots clés : acide déhydroacétique, pyrazoles, réaction de Vilsmeier–Haack, 3-acétyl-4-hydroxy-6-méthyl-2*H*-pyran-2-one.

[Traduit par la Rédaction]

Introduction

Significant interest in the chemistry of pyrazoles is reflected by the design of new synthetic approaches, theoretical calculations on the reactions leading to their formation, applications of new spectroscopic techniques and their significance in pharmaceuticals, agrochemicals, and dye stuffs, etc. (1–3). In the course of our studies on the synthesis of heterocyclic compounds from the reactions of dehydroacetic acid (DHA) and its derivatives (4–6), we have reported the synthesis of pyrazoles (**2**) and bipyrazoles (**3**) from the rearrangement of hydrazones of DHA (**1**) (7) (Scheme 1).

In the conversion of **1** to **2**, there is involvement of the pyrone ring of DHA, leading to the formation of a β-dicarbonyl moiety through a novel rearrangement process. In continuation of our studies dealing with the synthesis and properties of new pyrazole derivatives, we became interested in the synthesis of the pyrazoles in which the pyrone moiety of the DHA remains intact. We now report herein the synthesis of pyrazoles **4** and **5** from DHA by using the Vilsmeier–Haack reagent.



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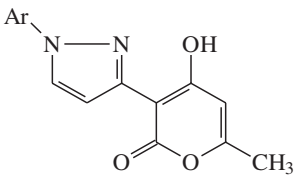

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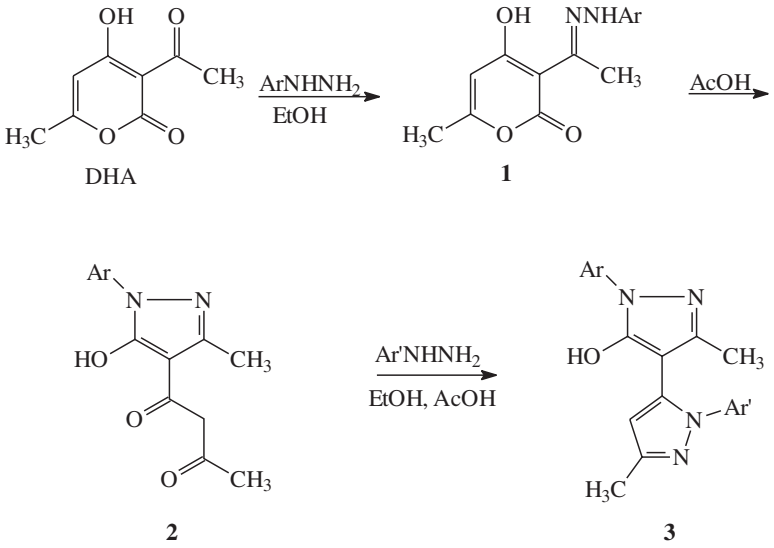
Scheme 1.



There are several recent reports involving the cyclization of some ketone hydrazones to 1-substituted 4-formylpyrazoles by using the Vilsmeier–Haack reagent ($POCl_3$–DMF, Scheme 2) (8–10). This transformation involves double formylation and its mechanistic pathways are not certain. Based on this important variation of the Vilsmeier–Haack reaction, we have adopted the same approach for the synthesis of **4**.

Scheme 2.

Results and discussion

1-Aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (1a–1e)

Initially, DHA phenylhydrazone (**1a**) was prepared by the condensation of phenylhydrazine and DHA in ethanolic solution containing a small amount of acetic acid, and was subjected to the Vilsmeier–Haack reaction under standard conditions, i.e., treating 2 equiv. of $POCl_3$–DMF with hydrazone **4a** at 55–60 °C for 5 h. The usual work up, followed by the purification of the resulting crude product by recrystallization from ethanol, gave the expected 4-formylpyrazole derivative **1a** as a crystalline solid in 75% yield. Similarly, several DHA hydrazones (**1b**–**1e**), which were obtained by treating DHA with arylhydrazines, also underwent the Vilsmeier–Haack reaction to afford the corresponding 1-aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (**4b**–**4e**) in good yields (Scheme 3). The structures of all products were established by their spectral properties, i.e., IR, ^{1}H NMR, MS, and elemental analyses.

The successful conversion of **3** to **4** reveals that the 4-hydroxy-6-methyl-2*H*-pyran-2-one system remains intact in the presence of the Vilsmeier–Haack reagent.

1-Aryl 3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (5a–5e)

After the successful conversion of **1** to **4**, we focused our attention on the synthesis of the related compounds **5**. The reaction was carried out using controlled conditions, such as the use of 1 equiv. of Vilsmeier–Haack reagent to carry out the monoformylation of hydrazone **1a** to generate the pyrazole **5a**. Interestingly, the reaction afforded the desired product 1-aryl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazole (**5a**), in 60% yield (Scheme 4). Using identical reaction conditions, syntheses of similarly constituted pyrazoles (**5b**–**5e**) were achieved.

To the best of our knowledge, all the reported cases of Vilsmeier–Haack reactions of hydrazones give 4-formylpyrazoles, as shown in Scheme 2. This study represents the first example of the preparation of pyrazoles **5** from the corresponding hydrazones.

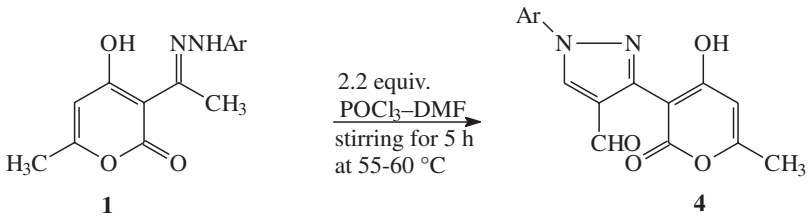
Conversion of 5 to 4

It is significant that pyrazoles **5a**–**5e** upon Vilsmeier–Haack reaction underwent smooth conversion into the corresponding 4-formylpyrazoles (**4a**–**4e**). The physical and spectral data of **4a**–**4e** were found to be identical with those obtained directly from **1**. The synthesis of **4** from **5**, not only provides additional examples of the Vilsmeier–Haack formylation of pyrazole derivatives, but also gives a clear indication of the involvement of **5** as an intermediate in the conversion of **1** to **4**.

Mechanistic pathways

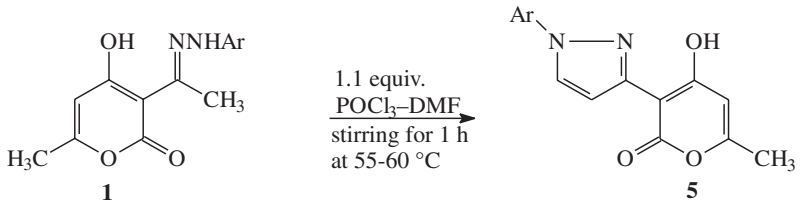
Although the mechanism of the Vilsmeier–Haack reaction is not certain, two alternative pathways (Scheme 5) can be envisaged. According to Scheme 5 (path a), formation of the products **4** involves double formylation at the CH_3 group of the hydrazones **1**, followed by cyclization. In the second pathway (path b), single formylation at the CH_3 group followed by cyclization, initially gives 4-unsubstituted pyrazoles (**5**), which subsequently undergo another formylation to produce **4**.

Scheme 3.



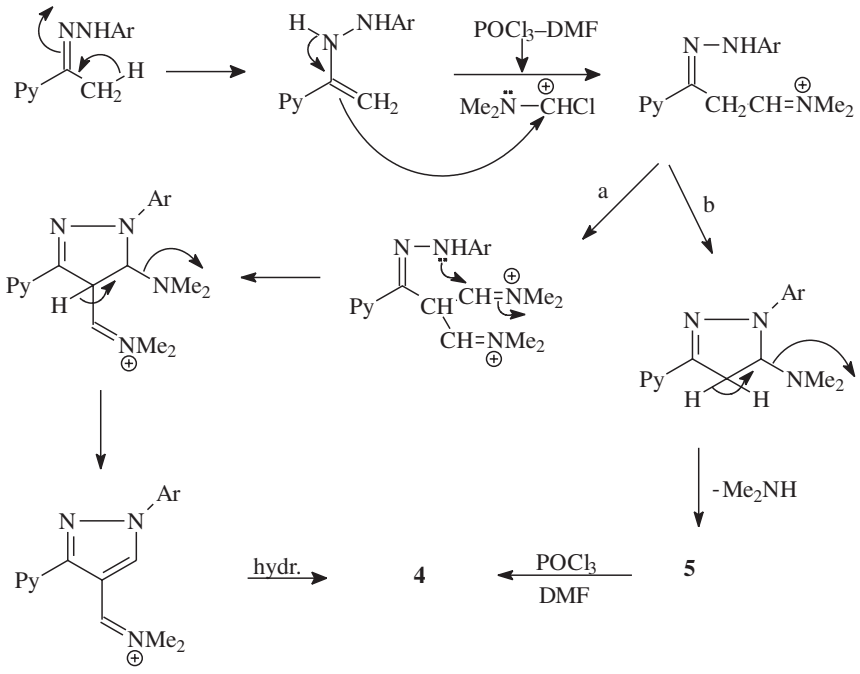
Compounds	Ar	Compounds	Ar
1a, 4a	C_6H_5	**1d, 4d**	4-$NO_2C_6H_4$
1b, 4b	4-$CH_3C_6H_4$	**1e, 4e**	2,4-$(NO_2)_2C_6H_3$
1c, 4c	4-ClC_6H_4		

Scheme 4.



Compounds	Ar	Compounds	Ar
1a, 5a	C_6H_5	**1d, 5d**	4-$NO_2C_6H_4$
1b, 5b	4-$CH_3C_6H_4$	**1e, 5e**	2,4-$(NO_2)_2C_6H_3$
1c, 5c	4-ClC_6H_4		

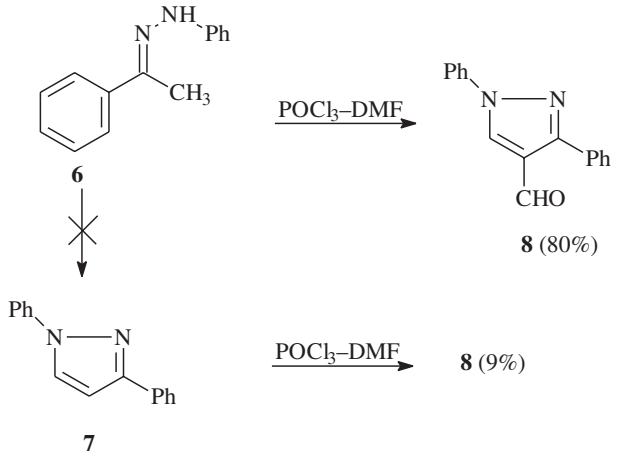
Scheme 5.



Since we were able to isolate the products **5** by using 1 equiv. of the Vilsmeier–Haack reagent (in this study), path b (Scheme 5) appears to be more reasonable. The observation in the present work that the second formylation of the pyrazole **5**, using similar reaction conditions and the reagent, indeed, afforded **4**, supports this pathway. However, in the presence of 2 equiv. of the Vilsmeier–Haack reagent, this study does not permit us to speculate on the operation of either of the two mechanisms as outlined in Scheme 5.

It is to be noted that in contrary to our observations, Kira

Scheme 6.



et al. (11) reported that in the case of Vilsmeier–Haack reaction of acetophenone phenylhydrazone (**6**), pyrazoles **7** are not intermediates in the reaction. They obtained 4-formyl-1,3-diphenylpyrazole (**8**) in 80% yield from the Vilsmeier–Haack reaction of **6**. However, formylation of 1,3-diphenylpyrazole (**7**) under identical conditions gave the same product (**8**), only in 9% yield (Scheme 6). Repetition of this work confirmed these observations.

Obviously, the presence of the 4-hydroxypyran-2-one moiety plays an important role in the conversions of **1** to **4** and of **5** to **4**. Further studies on related examples might be helpful to determine the actual effect of structural changes on the mechanistic pathways of these transformations.

Finally, noteworthy features of the present study are as follows:

(*i*) New pyrazole derivatives of **4** and **5** containing the 2-pyrone moiety are available through the Vilsmeier–Haack reaction using a simple experimental procedure. The mild reaction conditions do not allow attack at other nucleophilic positions (C(6) and C(4)-OH) of the pyrone moiety.

(*ii*) The synthesis of **5** represents the first example of monoformylation in the Vilsmeier–Haack reaction of the hydrazones of the $R(CH_3)C{:}NNHAr$ type.

(*iii*) The isolation of **5** and its subsequent formylation provides a valuable clue regarding the mechanistic pathways followed in these transformations.

(*iv*) The new pyrazole derivatives **4** and **5**, synthesized in the present work, are needed as precursors for the synthesis of several novel fused pyrazoloquinolone derivatives, particularly through the use of hypervalent iodine reagents.

Experimental

Instrumentation and general procedures

Melting points were taken in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument using TMS as an internal standard. IR spectra were recorded on a Buck Scientific IR M500 spectrophotometer. Elemental analyses were carried out in a PerkinElmer 2400 instrument, and mass spectra were recorded on a Kratos MS-50 mass spectrometer. Most of the common chemicals such as dehydroacetic acid, aldehydes, phenylhydrazine, 2,4-dinitrophenylhydrazine, etc., were obtained from commercial suppliers.

General procedure for the preparation of the hydrazone of DHA

DHA (0.02 molar equiv.) was dissolved in ethanol (50 mL) by warming, and arylhydrazine (0.02 molar equiv.) was added to the mixture while it was being shaken. The contents were stirred for 10 min and allowed to stand at room temperature for 2 h. The yellow solid (**1**) obtained was filtered and crystallized from acetonitrile.

Compounds **1a**–**1e** were similarly prepared.

General procedure for the preparation of 1-aryl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (5)

Hydrazone **1** (0.004 molar equiv.) was added to the Vilsmeier–Haack reagent (prepared from DMF (10 mL) and $POCl_3$ (0.0044 molar equiv.)), and the reaction mixture was stirred at 55–60 °C for 1 h and then poured into ice-cold water. The solid that separated upon neutralization with $NaHCO_3$ was filtered, washed with water, and crystallized from ethanol to afford **5**.

Compounds **5a**–**5e** were similarly prepared.

*3-(4-Hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-1-phenylpyrazole (5a)*

Yield: 65%; mp 158 to 159 °C. IR (KBr, cm^{-1}): 1720 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.3 (d, 1H, C_4-H, J = 2.1 Hz), 7.31 (m, 1H, Ph), 7.50 (m, 2H, Ph), 7.62 (m, 2H, Ph), 8.0 (d, 1H, C_5-H, J = 2.1 Hz), 13.0 (s, 1H, OH). MS *m*/*z*: 268. Elemental anal. calcd. for $C_{15}H_{12}N_2O_3$: C 67.16, H 4.48, N 10.44; found: C 67.28, H 4.49, N 10.34.

*3-(4-Hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-1-(4-tolyl)pyrazole (5b)*

Yield 60%; mp 122 to 123 °C. IR (KBr, cm^{-1}): 1723 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.3 (s, 3H, CH_3), 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.3 (d, 1H, C_4-H, J = 2.1 Hz), 7.0 (d, 2H, Ph, J = 8.0 Hz), 7.1 (d, 2H, Ph, J = 8.0 Hz), 8.0 (d, 1H, C_5-H, J = 2.1 Hz), 13.0 (s, 1H, OH). MS *m*/*z*: 282. Elemental anal. calcd. for $C_{16}H_{14}N_2O_3$: C 68.08, H 4.96, N 9.92; found: C 68.24, H 4.95, N 9.94.

*1-(4-Chlorophenyl)-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazole (5c)*

Yield 62%; mp 167 to 168 °C. IR (KBr, cm^{-1}): 1722 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.3 (d, 1H, C_4-H, J = 2.1 Hz), 7.1 (d, 2H, Ph, J = 8.1 Hz), 7.4 (d, 2H, Ph, J = 8.1 Hz), 8.0 (d, 1H, C_5-H, J = 2.1 Hz), 13.0 (s, 1H, OH). MS *m*/*z*: 302 (M^+), 304 (M^+ + 2). Elemental anal. calcd. for $C_{15}H_{11}ClN_2O_3$: C 59.50, H 3.63, N 9.25; found: C 59.53, H 3.64, N 9.29.

*3-(4-Hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-1-(4-nitrophenyl)pyrazole (5d)*

Yield 68%; mp 204 to 205 °C. IR (KBr, cm^{-1}): 1725 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.3 (d, 1H, C_4-H, J = 2.1 Hz), 7.6 (d, 2H, Ph, J = 8.4 Hz), 8.3 (d, 2H, Ph, J = 8.4 Hz), 8.0 (d, 1H,

C_5-H, J = 2.1 Hz), 13.0 (s, 1H, OH). MS *m/z*: 313. Elemental anal. calcd. for $C_{15}H_{11}N_3O_5$: C 57.51, H 3.51, N 13.42; found: C 57.55, H 3.49, N 13.44.

1-(2,4-Dinitrophenyl)-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)pyrazole (5e)

Yield 60%; mp 221 to 222 °C. IR (KBr, cm^{-1}): 1728 (C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.3 (d, 1H, C_4-H, J = 2.1 Hz), 7.6 (m, 1H, Ph), 8.3 (d, 1H, Ph), 8.7 (s, 1H, Ph), 8.0 (d, 1H, C_5-H, J = 2.1 Hz), 13.0 (s, 1H, OH). MS *m/z*: 358. Elemental anal. calcd. for $C_{15}H_{10}N_4O_7$: C 50.27, H 2.79, N 15.64; found: C 50.30, H 2.77, N 15.60.

General procedure for the preparation of 1-aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (4)

Hydrazone **1** (0.004 molar equiv.) was added to the Vilsmeier–Haack reagent (prepared from DMF (10 mL) and $POCl_3$ (0.0088 molar equiv.)), and the reaction mixture was stirred at 55–60 °C for 5 h and then poured into ice-cold water. The solid that separated upon neutralization with $NaHCO_3$ was filtered, washed with water, and crystallized from ethanol to afford **4**.

Compounds **4a**–**4e** were similarly prepared.

4-Formyl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-phenylpyrazole (4a)

Yield 55%; mp 118 to 119 °C. IR (KBr, cm^{-1}): 1720, 1683 (C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.0–7.7 (m, 5H, Ph), 8.5 (s, 1H, C_5-H), 9.9 (s, 1H, CHO), 13.0 (s, 1H, OH). MS *m/z*: 296. Elemental anal. calcd. for $C_{16}H_{12}N_2O_4$: C 64.86, H 4.05, N 9.45; found: C 64.88, H 4.06, N 9.44.

4-Formyl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-(4-tolyl)pyrazole (4b)

Yield 51%; mp 133 to 134 °C. IR (KBr, cm^{-1}): 1723, 1687 (C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.3 (s, 3H, CH_3), 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.0 (d, 2H, Ph, J = 8.0 Hz), 7.1 (d, 2H, Ph, J = 8.0 Hz), 8.5 (s, 1H, C_5-H), 9.9 (s, 1H, CHO), 13.0 (s, 1H, OH). MS *m/z*: 310. Elemental anal. calcd. for $C_{17}H_{14}N_2O_4$: C 65.80, H 4.51, N 9.03; found: C 65.81, H 4.49, N 9.06.

1-(4-Chlorophenyl)-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)pyrazole (4c)

Yield 52%; mp 143 to 144 °C. IR (KBr, cm^{-1}): 1722, 1686 (C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.1 (d, 2H, Ph, J = 8.1 Hz), 7.4 (d, 2H, Ph, J = 8.1 Hz), 8.5 (s, 1H, C_5-H), 9.9 (s, 1H, CHO), 13.0 (s, 1H, OH). MS *m/z*: 330 (M^+), 332 ($M^+ + 2$). Elemental anal. calcd. for $C_{16}H_{11}ClN_2O_4$: C 58.09, H 3.32, N 8.47; found: C 58.08, H 3.34, N 8.44.

4-Formyl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-(4-nitrophenyl)pyrazole (4d)

Yield 58%; mp 180 to 181 °C. IR (KBr, cm^{-1}): 1725, 1687 (C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.6 (d, 2H, Ph, J = 8.4 Hz), 8.3 (d, 2H, Ph, J = 8.4 Hz), 8.5 (s, 1H, C_5-H), 9.9 (s, 1H, CHO), 13.0 (s, 1H, OH). MS *m/z*: 341. Elemental anal. calcd. for $C_{16}H_{11}N_3O_6$: C 56.30, H 3.23, N 12.32; found: C 56.28, H 3.24, N 12.34.

1-(2,4-Dinitrophenyl)-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)pyrazole (4e)

Yield 55%; mp 200 to 202 °C. IR (KBr, cm^{-1}): 1728, 1685 (C=O). ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.4 (s, 3H, CH_3), 6.0 (s, 1H, C_5-H, DHA), 7.6 (m, 1H, Ph), 8.3 (d, 1H, Ph), 8.8 (s, 1H, Ph), 8.5 (s, 1H, C_5-H), 9.9 (s, 1H, CHO), 13.0 (s, 1H, OH). MS *m/z*: 386. Elemental anal. calcd. for $C_{15}H_{12}N_2O_3$: C 67.16, H 4.48, N 10.44; found: C 49.28, H 4.49, N 10.34.

General procedure for the preparation of 1-aryl-4-formyl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazoles (4) from 1-aryl-3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)pyrazole (5)

Compound **5** (0.004 molar equiv.) was added to the Vilsmeier–Haack reagent (prepared from DMF (10 mL) and $POCl_3$ (0.0044 molar equiv.)), and the reaction mixture was stirred at 55–60 °C for 4 h and then poured into ice-cold water. The solid that separated upon neutralization with $NaHCO_3$ was filtered, washed with water, and crystallized from ethanol to afford **4** in 50% yields.

Compounds **4a**–**4e** were similarly prepared.

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