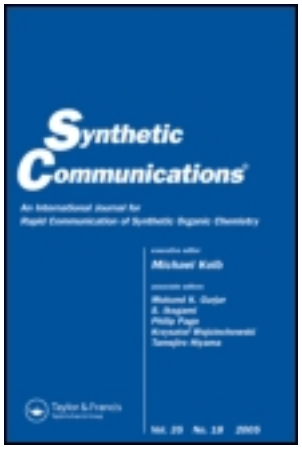

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4,6-Diacetylresorcinol in Heterocyclic Synthesis, Part I: Synthesis and Biological Evaluation of Some New Linearly and Angularly Substituted Pyrano[3,2-g] Chromenes via Vilsmeier-Haack Formylation of 4,6-Diacetylresorcinol, Its Schiff Bases, and Hydrazones

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4,6-DIACETYLRESORCINOL IN HETEROCYCLIC SYNTHESIS, PART I: SYNTHESIS AND BIOLOGICAL EVALUATION OF SOME NEW LINEARLY AND ANGULARLY SUBSTITUTED PYRANO[3,2-*g*] CHROMENES VIA VILSMEIER–HAACK FORMYLATION OF 4,6-DIACETYLRESORCINOL, ITS SCHIFF BASES, AND HYDRAZONES

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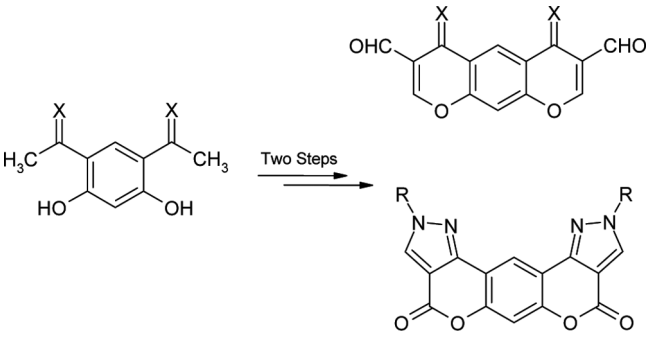
GRAPHICAL ABSTRACT



Abstract *Application of Vilsmeier–Haack reaction on 4,6-diacetylresorcinol (**1**) led to the formation of 4,6-dioxo-4*H,6H-*pyrano[3,2-*g*]chromene-3,7-dicarboxaldehyde (**2**) in good yield. The dicarboxaldehyde **2** was condensed with some carbon and nitrogen nucleophiles. Some aliphatic and aromatic Schiff bases of 4,6-diacetylresorcinol (**1**) were subjected to Vilsmeier–Haack formylation reaction to afford 4,6-*bis*(alkyl/arylimino)-4*H,6H-*pyrano[3,2-*g*]chromene-3,7-dicarbaldehydes **10, 14**, and **15**. Also, treatment of some* bis-*hydrazones of 4,6-diacetylresorcinol **16–19** with Vilsmeier–Haack reagent afforded the corresponding 4,6-*bis*(4-formylpyrazol-3-yl)resorcinols **20** and **21**, which underwent oxidation with iodine to yield the pyrano[3,2-*g*]chromeno[4,3-*c*:7,6-*c*]dipyrazole-4,8-diones **22** and **23**, respectively. Most of the synthesized compounds revealed weak antimicrobial activities. It was noticed that the dicarboxaldehydes **2, 10, 14,** and **15** exhibited moderate antibacterial activity against Gram-positive bacteria, yeast, and fungus.*

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[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Antimicrobial activities; 4,6-diacetylresorcinol; pyrano[3,2-*g*]chromenes; Vilsmeier–Haack formylation

INTRODUCTION

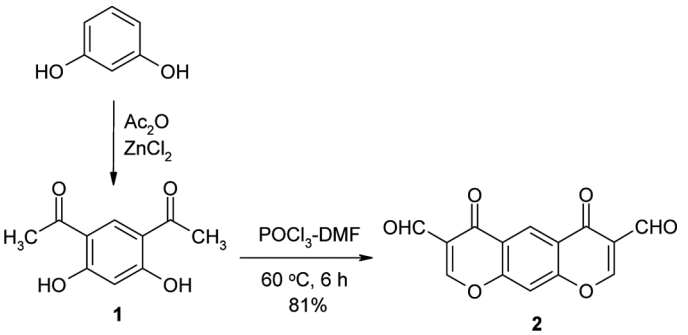
The Vilsmeier–Haack reaction is a widely used method for the formylation of activated aromatic and heteroaromatic compounds.[1,2] The reactions of aliphatic substrates, particularly carbonyl compounds[3,4] with chloromethyleneiminium salts, led to multiple iminoalkylations in the presence of excess reagent and the resulting intermediates underwent cyclization to afford aromatic or heterocyclic compounds.[5] Multifunctional intermediates derived from these reactions (e.g., β-chloroenaldehydes) are subsequently exploited for the synthesis of functionalized heterocycles or other valuable target molecules.[6] Dibenzyl ketone on treatment with chloromethyleneiminium salt underwent multiple iminoalkylations followed by cyclization to afford 3,5-diphenyl-4*H*-pyran-4-one.[7] Furthermore, the reactions of 2-hydroxyacetophenones with Vilsmeier–Haack reagent also involve an iminoalkylation cyclization sequence, leading to the formation of 3-formylchromones.[8–10]

The chromone and coumarin derivatives are found in the molecular structure of many important natural secondary metabolites[11,12] and compounds with high pharmacological activity.[13,14] The incorporation of a fused heterocyclic moiety in the parent chromone and coumarin alters their properties and converts them into more important derivatives.[15,16] Large numbers of heterocycles fused with chromone and coumarin are used as drugs and dyes.[17,18]

In our recent work, we have demonstrated the utility of the Vilsmeier–Haack reagent in the synthesis of functionalized heterocyclic systems such as pyrazoles, chromeno[4,3-*c*]pyrazoles, and chromeno[2,3-*g*]indazoles.[19] Thus, as a continuation of our research interest in the synthesis of highly valuable heterocycles,[20,21] we prepared 4,6-diacetylresorcinol, its Schiff bases and hydrazones followed by examination of their reactivities toward Vilsmeier–Haack reagent. Also, the preliminary antimicrobial activities of the synthesized compounds were screened.

RESULTS AND DISCUSSION

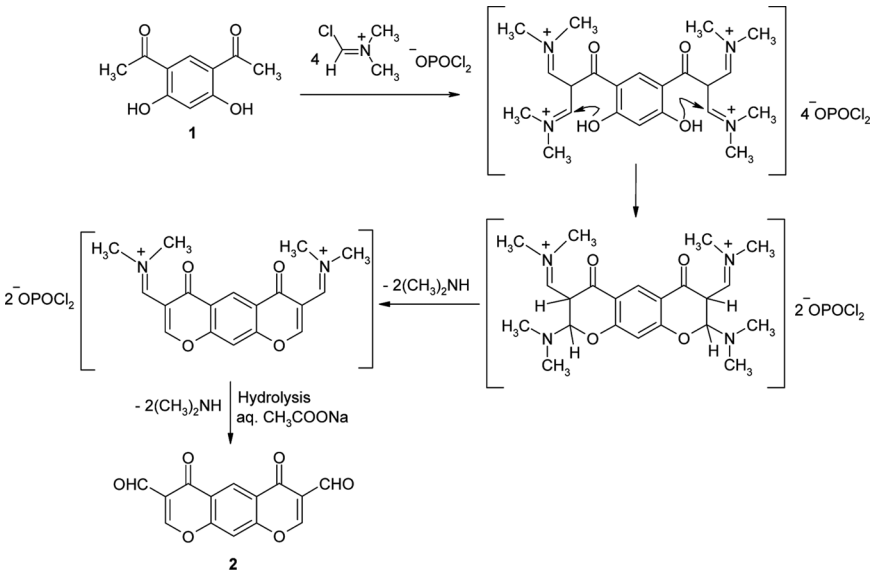
4,6-Diacetylresorcinol (**1**) was prepared in excellent yield via acetylation of resorcinol with acetic anhydride in the presence of freshly fused zinc chloride according to the previously reported procedure (Scheme 1).[22] Application of Vilsmeier–Haack reaction on the substrate **1** afforded 4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*] chromene-3,7-dicarboxaldehyde (**2**) in good yield (Scheme 1). It may be mentioned here that compound **2** was obtained by Mallaiah and Srimannarayana [23] in poor yield. However, no full spectral characterization of this product was made. The proposed mechanism for the formation of **2** involved double formylation at each methyl group of **1**, followed by self-cyclization and then hydrolysis in basic medium (Scheme 2).[24] The infrared (IR) spectrum of compound **2** showed three characteristic absorption bands



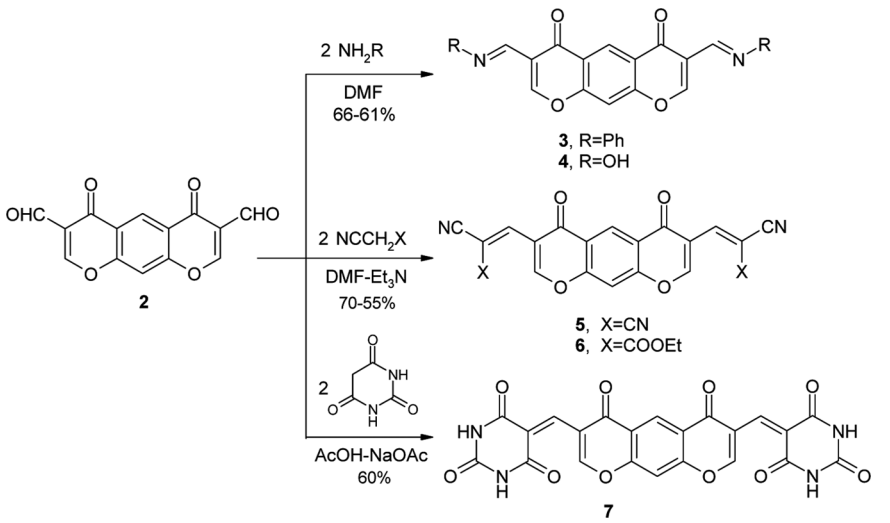
Scheme 1. Formation of 4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-dicarboxaldehyde (**2**) via Vilsmeier–Haack reaction of the substrate **1**.

at 1707, 1655, and 1625 cm^{-1} assignable to CHO, C=O_{pyrone}, and C=C functions, respectively. The ^{1}H NMR spectrum of compound **2** exhibited a singlet at δ 10.10 ppm for the formyl protons and the protons of the pyrone rings in position 2 resonated at δ 8.76 ppm. In addition, two singlets were present at δ 7.94 and 9.02 ppm corresponding to the protons H-10 and H-5, respectively.[25] Furthermore, its mass spectrum revealed the molecular ion peak at m/z 270 (M^+), which agreed with the suggested molecular formula.

The chemical reactivity of 4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-dicarboxaldehyde (**2**) was studied via its simple condensation reactions with some carbon and nitrogen nucleophiles. Thus, compound **2** was condensed with aniline and hydroxylamine hydrochloride in dry dimethylformamide (DMF) to give moderate yields of the corresponding *bis*-azomethine **3** and *bis*-oxime **4**, respectively



Scheme 2. Proposed mechanism of the formation of compound **2**.

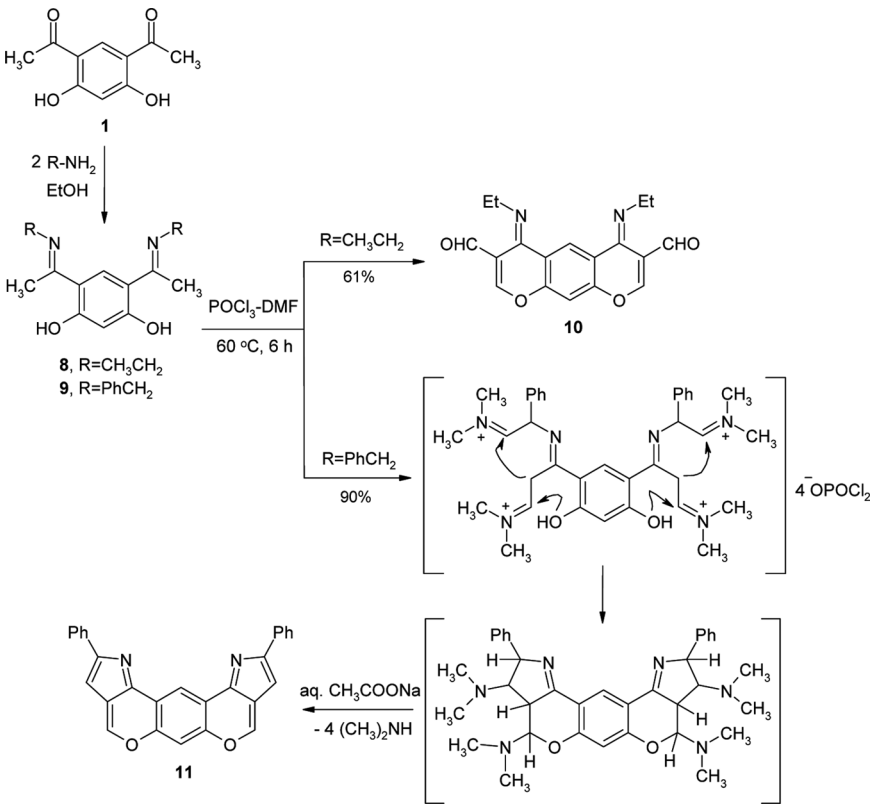


Scheme 3. Condensation reactions of dicarboxaldehyde **2** with some nitrogen and carbon nucleophiles.

(Scheme 3). The IR spectra of compounds **3** and **4** clearly showed disappearance of the aldehyde absorption band, and new bands at δ 1594 and 1629 cm^{-1} appeared for imino groups for them, respectively. The ^1H NMR spectrum of **4** showed the OH signal at δ 12.74 ppm in addition to the protons H-5, CH=N, and H-10 appeared at δ 8.89, 7.95, and 7.48 ppm, respectively.

The Knoevenagel condensation reaction of compound **2** with acyclic and cyclic active methylene groups was studied. Thus, the reaction of **2** with malononitrile and ethyl cyanoacetate in dry DMF containing a few drops of triethylamine afforded 2,2′-[(4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-diyl)dimethylidene]dipropanedinitrile (**5**) and diethyl 3,3′-[(4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-diyl)]-*bis*(2-cyanoprop-2-enoate) (**6**), respectively (Scheme 3). Similarly, condensation of **2** with barbaturic acid as cyclic active methylene compound in glacial acetic acid and freshly fused sodium acetate yielded 5,5′-[(4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-diyl)dimethylidene]dipyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (**7**) (Scheme 3). The assigned structures of **5**–**7** were confirmed by the correct elemental analysis in addition to the spectral data. Their IR spectra revealed characteristic absorption bands at region 2220 – 2192 cm^{-1} for nitrile groups in compounds **5** and **6**, in addition to the characteristic absorption bands for the carbonyl groups of **6** and **7** appeared at 1733 ($C{=}O_{ester}$) and 1707 ($C{=}O_{amide}$) cm^{-1}, respectively. The ^1H NMR spectrum of **6** showed the ethoxy protons at δ 1.22 (CH_3) and 4.19 ppm (CH_2), whereas compound **7** revealed the NH protons as broad signal at δ 11.50 ppm and the exocyclic CH=C protons as singlet at δ 6.94 ppm.

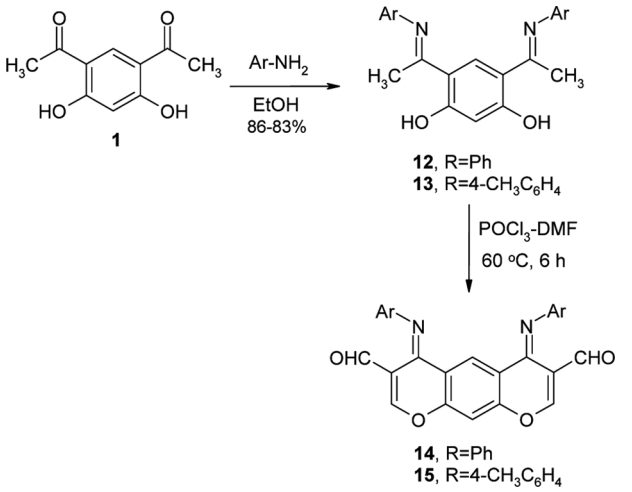
We selected some aliphatic and aromatic Schiff bases of 4,6-diacetylresorcinol as model compounds to examine their chemical behavior under Vilsmeier–Haack formylation conditions. Thus, treatment of 4,6-*bis*[1-(ethylimino)ethyl]resorcinol (**8**) and 4,6-*bis*[1-(benzylimino)ethyl]resorcinol (**9**) with Vilsmeier–Haack reagent afforded 4,6-*bis*(ethylimino)-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-dicarbaldehyde (**10**) and 2,10-diphenylpyrano[3,2-*g*]chromeno[4,3-*b*:7,6-*b*]dipyrrole (**11**), respectively



Scheme 4. Vilsmeier–Haack formylation of aliphatic Schiff bases of 4,6-diacetylresorcinol **8** and **9**.

(Scheme 4). The proposed mechanism for the formation of **10** involved double formylation at each methyl group of acetyl groups in compound **8**, followed by self-cyclization and then hydrolysis in basic medium as occurred in the formation of **2**. Also, the proposed mechanism for the formation of **11** involved monoformylation at each methyl and methylene groups of **9**, followed by self-cyclization and then hydrolysis in basic medium (Scheme 4). The analytical and spectroscopic data proved the proposed structures of **10** and **11**. Their IR spectra revealed the formyl groups at 1704 cm^{-1} in compound **10** while it was absent in compound **11**. The ^{1}H NMR spectrum of **10** showed the aldehydic protons at δ 10.08 ppm and the ethyl groups at δ 1.20 (CH_3) and 4.25 (CH_2). Furthermore, the ^{1}H-NMR spectrum of **11** did not show any aldehydic proton but showed the H−3 proton of pyrrole rings at δ 7.90 ppm, which supports the cyclization process. The mass spectra of compounds **10** and **11** showed the parent ion peaks at m/z 266 (M−2Et) and 412 (M^+), respectively.

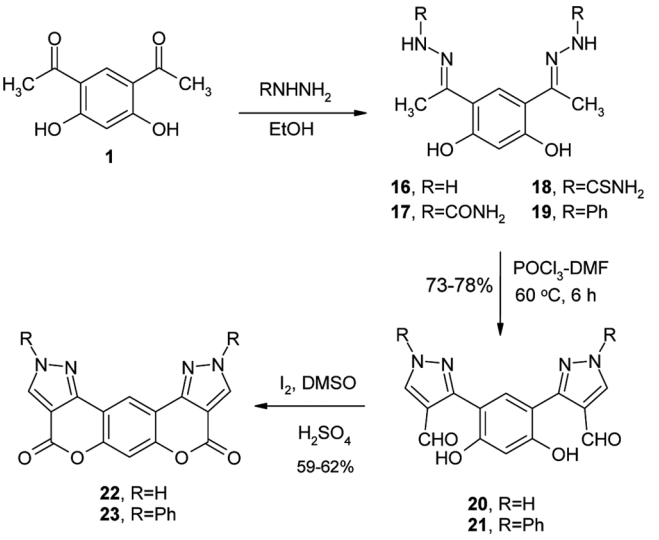
On the other hand, the novel 4,6-*bis*(phenylimino)-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-dicarbaldehyde (**14**) and 4,6-*bis*(4-methylphenylimino)-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-dicarbaldehyde (**15**) were obtained from treatment of 4,6-*bis*[1-(phenylimino)ethyl]resorcinol (**12**) and 4,6-*bis*[1-(4-methylphenylimino)-ethyl]resorcinol (**13**), respectively, with Vilsmeier–Haack reagent (Scheme 5). The



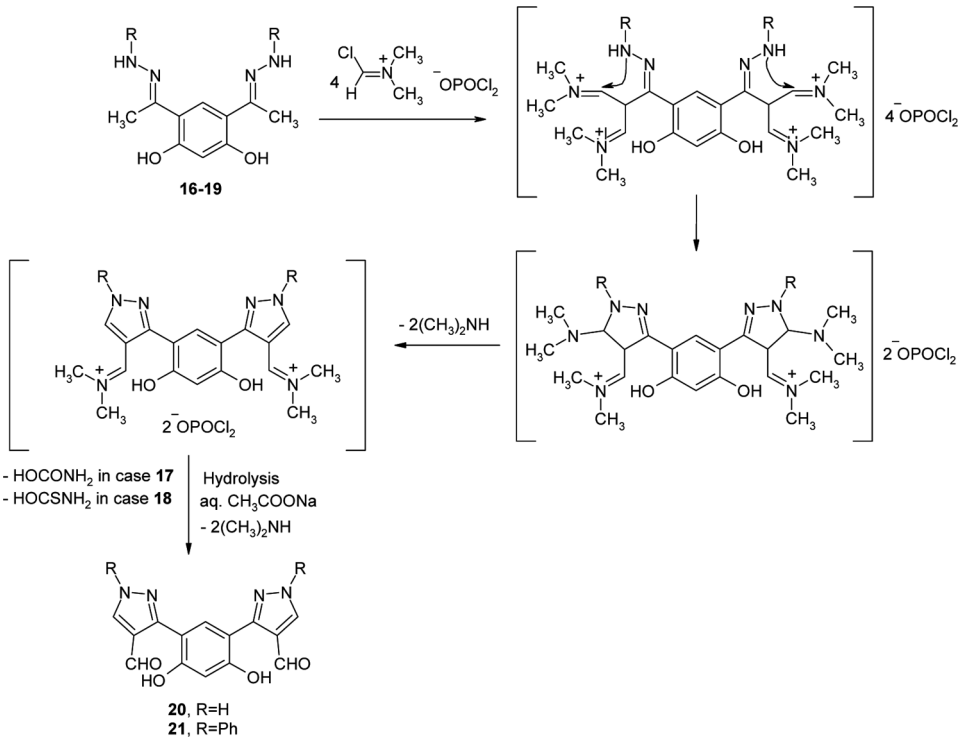
Scheme 5. Vilsmeier–Haack formylation of aromatic Schiff bases of 4,6-diacetylresorcinol **12** and **13**.

proposed mechanism for the formation of compounds **14** and **15** involved double formylation at each methyl group of acetyl groups **8**, followed by self-cyclization and then hydrolysis in basic medium as occurred in formation of **2** and **10**. The IR spectra of **14** and **15** showed strong absorption bands at 1690 and 1698 cm^{-1} assignable to CHO groups, respectively. Their ^1H NMR spectra exhibited singlets at δ 10.20 and 10.11 ppm for the formyl protons, respectively. The protons of the pyrone rings in position 2 resonated at δ 8.51 and 9.07 ppm, respectively. Moreover, their mass spectral data revealed their molecular ion peaks at m/z 420 and 448, respectively.

The present work was also extended to apply the Vilsmeier–Haack formylation reaction on some hydrazones of 4,6-diacetylresorcinol that led to new 4,6-*bis*(4-formylpyrazol-3-yl)resorcinol systems. Thus, the *bis*-hydrazone **16**, *bis*-semicarbazone **17**, and *bis*-thiosemicarbazone **18** were treated with Vilsmeier–Haack reagent under the previous conditions to afford only one, a pale brown crystalline product named, 4,6-*bis*(4-formyl-1*H*-pyrazol-3-yl)resorcinol (**20**) (Scheme 6).[26] Formation of compound **20** involved double formylation at the methyl groups of compounds **16–18** followed by nucleophilic attack of NH groups at $–CH=N^+(CH_3)_2$ moieties to eliminate two molecules of dimethylamine. The basic hydrolysis removes the amide and thioamide moieties to give the final product **20** (Scheme 7). The spectral data of **20** supported the proposed structure because its ^1H NMR spectrum displayed a broad singlet (D_2O exchangeable) at δ 12.50 ppm due to NH and OH protons and a singlet at δ 9.80 ppm due to the aldehydic protons. The H-5 protons of the formed pyrazole rings were also observed at δ 8.41 ppm. Also, its IR spectrum showed very a broad absorption band at 3119 cm^{-1} due to NH and OH groups and a strong band for the aldehyde groups at 1692 cm^{-1}. Similarly, when the *bis*-phenylhydrazone **19** was subjected to Vilsmeier–Haack reagent, it gave 4,6-*bis*(4-formyl-1-phenylpyrazol-3-yl)resorcinol (**21**) (Scheme 6). The structure of **21** was proved by the analytical and spectroscopic data. Its ^1H NMR spectrum



Scheme 6. Formation of compounds **20**–**23** from their hydrazones **16**–**19**.



Scheme 7. Proposed mechanism for formation of compounds **20** and **21** from their hydrazones **16**–**19**.

displayed the aldehydic protons at δ 9.85 ppm and H-5 of pyrazole rings at δ 9.21 ppm, respectively. The mass spectrum of **21** recorded the molecular ion peak at m/z 450 (66%), which agreed with the molecular formula of the proposed structure.

The oxidation reaction of compounds **20** and **21** with iodine in dimethylsulfoxide (DMSO) containing a few drops of concentrated sulfuric acid[27] afforded the new fused angularly polyheterocyclic systems, namely, pyrano[3,2-*g*]chromeno [4,3-*c*:7,6-*c*]dipyrazole-4,8-(4*H*) dione (**22**) and 2,10-diphenylpyrano[3,2-*g*]chromeno [4,3-*c*:7,6-*c*]dipyrazole-4,8-(4*H*)dione (**23**), respectively (Scheme 6). The absorption bands of the carbonyl groups appeared at 1716 and 1752 cm^{-1} in the IR spectra of **22** and **23**, respectively. Also, their structures were confirmed from ^{1}H-NMR spectra by disappearance of OH and CHO protons in compounds **20** and **21** (see the experimental section). Finally, the molecular ion peaks of **22** and **23** were recorded in accordance with their molecular formulas.

ANTIMICROBIAL EVALUATION

The newly synthesized target compounds were evaluated for their in vitro antibacterial activity against *Staphylococcus aureus* (ATCC 25923) and *Bacillus subtilis* (ATCC 6635) as example of Gram-positive bacteria and *Escherichia coli* (ATCC 25922) and *Salmonella typhimurium* (ATCC 14028) as examples of Gram-negative bacteria. They were also evaluated against *Candida albicans* (ATCC 10231) as yeast and the fungus *Aspergillus fumigatus*. Agar diffusion technique was used for the determination of the preliminary antibacterial and antifungal activities.[28] The test was performed on medium potato dextrose agar (PDA), which contained infusion of 200 g potatoes, 6 g dextrose, and 15 g agar. Uniform-size filter paper disks (three disks per compound) were impregnated by equal volume (10 µl) from the concentrations of 500 and 1000 µg/mL dissolved compounds in dimethylformamide (DMF) and carefully placed on inoculated agar surface after incubation for 36 h at 27 °C in the case of bacteria and for 48 h at 24 °C in the case of fungi. Cephalothin, chloramphenicol and cycloheximide were used as reference drugs for Gram-positive bacteria, Gram-negative bacteria, and yeast and the fungus, respectively. The obtained results were recorded for each tested compound as average diameter of inhibition zones of the bacteria, yeast, and fungus around the disks in mm at the concentrations 500 and 1000 µg/mL. The antimicrobial activities were determined by measuring the inhibition zones (Table 1).

1. The results depicted in Table 1 revealed that the most of tested compounds displayed variable inhibitory effects on the growth of the tested Gram-positive and Gram-negative bacterial strains, and also against yeast and fungus.
2. In general, most of the tested compounds revealed weak activities against the microorganism strains.
3. It was noticed that pyrano[3,2-*g*]chromene-3,7-dicarboxaldehydes **2, 10, 14**, and **15** exhibited moderate antibacterial activity against Gram-positive bacteria, yeast, and fungus.
4. Regarding the structure–activity relationship of the formed *bis*-aldehydes **2, 10, 14**, and **15**, the results revealed that compound **2** exhibited a good activity profile, which indicated that $C{=}O_{pyrone}$ is more effective than $C{=}N_{azomethine}$ groups.

Table 1. In vitro antimicrobial activities of the synthesized compounds **2–23** at 500 and 1000 μg/mL by disc diffusion assay

		Zone of inhibition (mm)[a]					
		Bacteria Gram (+) ve		Bacteria Gram (–) ve		Yeast	Fungi
Compound	Concentration (μg/ml)	*S. aureus*	*B. subtilis*	*E. coli*	*S. typhimurium*	*C. albicans*	*A. fumigatus*
2	500	18	13	—	—	19	20
	1000	21	19	—	—	25	23
3	500	8	—	7	7	—	—
	1000	10	—	9	10	—	—
4	500	—	—	7	—	—	—
	1000	—	—	9	—	—	—
5	500	—	—	—	8	—	—
	1000	—	—	—	10	—	—
6	500	—	—	—	—	—	—
	1000	—	—	—	—	—	—
7	500	—	—	7	8	—	—
	1000	—	—	9	9	—	—
10	500	12	10	—	—	19	16
	1000	15	13	—	—	25	19
11	500	—	—	—	—	—	—
	1000	—	—	—	—	—	—
14	500	12	9	—	—	8	16
	1000	14	13	—	—	13	19
15	500	12	10	—	—	16	18
	1000	18	14	—	—	20	22
20	500	8	—	—	8	—	—
	1000	8	—	—	10	—	—
21	500	—	—	—	—	16	—
	1000	—	—	—	—	20	—
22	500	14	13	—	—	12	14
	1000	17	16	—	—	17	16
23	500	11	12	—	—	13	16
	1000	15	16	—	—	15	19
Standard drug	500	26	25	28	27	28	26
	1000	35	35	36	38	35	37

[a]Low activivity, 6–12 mm; moderate activity, 13–19 mm; high activity, 20–30 mm. —, no inhibition or inhibition less than 5 mm.

5. Conversion of pyrano[3,2-*g*]chromene-3,7-dicarboxaldehydes **2** to other derivatives **3**–**7** unfortunately produced very weak antimicrobial activities, which indicated that $C{=}O_{formyl}$ is more effective than the exocyclic C=N and C=C groups.
6. On the other hand, pyrano[3,2-*g*]chromeno[4,3-*c*:7,6-*c*]dipyrazole-4,8-(4*H*)diones **22** and **23** recorded moderate activities against the tested microorganisms except Gram-negative bacteria.
7. In conclusion, the objective of the present study was to synthesize and investigate the antimicrobial activities of some new functionalized 4,6-dixo- and 4,8-dioxo-pyrano[3,2-*g*]chromenes with the hope of discovering new structure leads for

antimicrobial agents. Generally, the prepared compounds showed lower to moderate activities. However, none of the tested compounds was as or more active than the reference drugs.

EXPERIMENTAL

The melting point was determined in an open capillary tube on a digital Stuart SMP-3 apparatus. Infrared spectra were measured on a Fourier transform infrared (FTIR) Nicolet IS10 spectrophotometer (cm^{-1}), using KBr disks. The ^1H NMR spectra were measured on Mercury-300BB (300 MHz), using DMSO-d_6 as a solvent and the chemical shifts δ downfield from tetramethylsilane (TMS) as an internal standard. The ^{13}C NMR spectra could not be measured for all these compounds because of their poor solubility in greater concentrations in most common solvents. Mass spectra were recorded on a gas chromatographic DI analysis Shimadzu instrument Q-2010 Plus at 70 eV. Elemental analyses were performed on Perkin-Elmer 2400II at the Chemical War Department, Ministry of Defense, Cairo, Egypt. All the *bis*-Schiff bases **8**,[29] **9**,[30] **12**,[31] **13**,[31] *bis*-hydrazones **16**,[32] and **19**,[32] and *bis*-(thio)semicarbazones **17**,[33] and **18**[33] were prepared according to the reported procedures in the literature.

Synthesis of Compounds 2, 10, 11, 14, 15, 20, and 21: General Procedure for Vilsmeier–Haack Formylation of 4,6-Diacetylresorcinol (1), *bis*-Schiff Bases 8, 9, 12, 13, and *bis*-Hydrazones 16–19

The Vilsmeier–Haack reagent was prepared by adding $POCl_3$ (60 mmol, 6 mL) dropwise to ice-cold dry DMF (30 mL) while stirring. The mixture was then stirred for 10–15 min at 0 °C. Each one of the compounds **1, 8, 9, 12, 13,** and **16–19** (10 mmol) was added as a solution in DMF (10 mL) to the Vilsmeier–Haack reagent. Then the mixture was stirred for 6 h at 60–70 °C. The reaction mixture was cooled and poured into crushed ice, and 3 g of sodium acetate was added under constant manual stirring. The reaction mixture was kept aside overnight. The resulting precipitate was filtered off and crystallized from DMF to give the corresponding products **2, 10, 11, 14, 15, 20,** and **21**, respectively.

Synthesis of Compounds 3 and 4: General Procedure for Condensation of 2 with Nitrogen Nucleophiles

A mixture of compound **2** (2.5 mmol, 0.67 g) and freshly distillated aniline and hydroxylamine hydrochloride (5 mmol) in dry dimethylformamide (25 ml) was heated under reflux for 6 h. After cooling, the formed precipitates were filtered off and crystallized from dimethylformamide to give the products **3** and **4**, respectively.

Synthesis of Compounds 5 and 6: General Procedure for Condensation of 2 with Acyclic Carbon Nucleophiles

A mixture of compound **2** (2.5 mmol, 0.67 g), malononitrile, and ethyl cyanoacetate (5 mmol) in dry dimethylformamide (25 ml) containing a few drops of

triethylamine was heated under reflux for 6 h. After cooling, the formed precipitates were filtered off and crystallized from dimethylformamide to give the products **5** and **6**, respectively.

Synthesis of 5,5′-[(4,6-Dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-diyl)dimethylidene] Dipyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (7)

A mixture of compound **2** (2.5 mmol, 0.67 g) and barbaturic acid (5 mmol, 0.32 g) in glacial acetic acid (25 ml) and freshly fused sodium acetate (2 g) was heated under reflux for 6 h. The reaction mixture was cooled, poured into crushed ice, and kept under constant manual stirring for 1 h. The resulting precipitate was filtered off, washed with water several times, and crystallized from dimethylformamide to give the product **7**.

Synthesis of Compounds 22 and 23: General Procedure for Oxidation of 20 and 21 with Iodine

Iodine (10 mol%) and four to five drops of concentrated sulfuric acid were added to a solution of each compound **20** and **21** (2.5 mmol) in dimethylsulfoxide (15 ml). The reaction mixture was heated under reflux at 120 °C for 10 h. The contents were cooled to room temperature and poured into ice-cooled water. The separated solids were filtered off and washed with diluted sodium thiosulfate solution. The obtained products were crystallized from dimethylformamide to give the products **22** and **23**, respectively.

SUPPORTING INFORMATION

Full characterization of the synthesized compounds and spectral data can be found via Supplementary Content section of this article's Web page.

CONCLUSION

An efficient one-pot synthesis of 4,6-dioxo-4*H*,6*H*-pyrano[3,2-*g*]chromene-3,7-dicarboxaldehyde (**2**) was achieved from application of Vilsmeier–Haack formylation on 4,6-diacetylresorcinol. This general protocol provides a novel and facile access to other substituted linearly and angularly pyrano[3,2-*g*]chromenes by sequential Vilsmeier–Haack formylation, intramolecular cyclization, and aromatization reactions of Schiff bases and hydrazones of 4,6-diacetylresorcinol.

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