**5-Benzyloxy-4-oxo-4H-pyran-2-carboxisopropylamide (VII)**

VI (0.0018 mol) was dissolved in minimum of absolute acetone. Isopropylamine (0.16 cm³) and triethylamine (0.27 cm³) were added. Mixture was stirred at laboratory temperature for 1 h, then mixed with excess of water and extracted with benzene. Evaporation of solvent gave solid product. Raw material was crystallized from benzene.

N-(4-Methylphenyl) amide of 5-benzyloxy-4-oxo-4H-pyran-2-carboxylic acid (IX) was prepared by analogous method.

**REFERENCES**

1. Robiquet, A., Ann. 5, 95 (1833).

Translated by J. Bransová

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**Synthesis and Antimycobacterial Effect of 3-Formylchromone N-Aroyl- or N-Alkylcarbonylhydrazones**

H. M. EL-SHAAER, M. LÁCOVÁ, Ž. ODLEROVÁ, and M. FURDÍK

*Department of Chemistry, Ain Shams University, Cairo, Egypt*
*Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, SK-842 15 Bratislava*
*Institute of Preventive Medicine, SK-833 01 Bratislava*

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3-Formylchromone N-aroyl- or N-alkylcarbonylhydrazones were prepared by condensation reaction of 3-formylchromones with hydrazine derivatives in ethanol and toluene-p-sulfonic acid as catalyst. Some of the prepared compounds were tested against typical and atypical *Mycobacterium tuberculosis*.

Biological activities of chromone derivatives render them of considerable pharmaceutical and chemical interest [1]. In this work we describe the synthesis of 3-formylchromone N-aroylhydrazones and 3-formylchromone N-alkylcarbonylhydrazones because many of hydrazide derivatives are of pharmacological importance [2], and also 3-formylchromones show interesting pharmacological activities [3—5], so we were interested to synthesize some new derivatives of chromones with prediction of new pharmacological activities.

4-Oxo-4H-1-benzopyrans in their reactions with phenylhydrazine behave like α,β-unsaturated ketones...
and the nucleophile attacks at C-2 (Michael addition) with the opening of the pyrone ring to give pyrazole derivatives [6, 7].

In our study we found that the 3-formylchromones (I) were reacted with hydrazide derivatives (II) in ethanol and toluene-p-sulfonic acid as catalyst at temperature 50—60 °C to give 3-formylchromone N-aroyl- or N-alkylcarbonylhydrazones (IIIa—Illp) (Scheme 1). The starting aldehydes for compounds IIIa, IIIc, and IIIp were prepared according to [8].

The structure of compounds IIIa—Illp was confirmed by IR spectra (Table 1) and $^1$H NMR spectra.

Table 1. Characteristic Data of Compounds III and IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>M&lt;sub&gt;r&lt;/sub&gt;</th>
<th>Yield (%)</th>
<th>m.p. °C</th>
<th>IR&lt;sup&gt;*&lt;sub&gt;, v/cm&lt;sup&gt;-1&lt;/sup&gt;&lt;/sub&gt;</th>
<th>Pyrrole</th>
<th>Amide</th>
<th>NH</th>
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<td>308.29</td>
<td>58</td>
<td>222—224</td>
<td>1620</td>
<td>1653</td>
<td>3251</td>
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<tr>
<td>IIIb</td>
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<td>50</td>
<td>198—201</td>
<td>1642</td>
<td>1700</td>
<td>3200</td>
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<tr>
<td>IIIc</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>1634</td>
<td>1690</td>
<td>3280</td>
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<tr>
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<td>240—242</td>
<td>1617</td>
<td>1649</td>
<td>3153</td>
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<td>49</td>
<td>239—240</td>
<td>1629</td>
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<td>250—252</td>
<td>1625</td>
<td>1694</td>
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<td>325.3</td>
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<td>254—255</td>
<td>1615</td>
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<td>71</td>
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<td>62</td>
<td>262—263</td>
<td>1612</td>
<td>1649</td>
<td>3150</td>
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<tr>
<td>IVa</td>
<td>C&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>73</td>
<td>279—281</td>
<td>—</td>
<td>—</td>
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<td>IVb***</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>220.1</td>
<td>68</td>
<td>304—306</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
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</table>

*In paraffin oil. **% CI w(calc.), w(found): 10.82, 10.87. ***IR for IVb v/cm<sup>-1</sup>: 3332 (br), 3465 (br) v(OH); 1610, 1615 v(C=N).
Table 2. $^1$H NMR spectra of Compounds IIle, IIlg, IIlh, IVa, and IVb

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$</th>
</tr>
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<tr>
<td>IIle</td>
<td>11.96 (s, 1H, NH), 8.80 (s, 1H, H-2), 8.63 (s, 1H, H-9), 6.92—8.06 (m, 7H, $H_{aron}$), 2.45 (s, 3H, CH$_3$)</td>
</tr>
<tr>
<td>IIlg</td>
<td>12.11 (s, 1H, NH), 8.65—8.82 (m, 4H, H-2, H-9, H-15), 7.64—7.91 (m, 5H, $H_{aron}$), 2.45 (s, 3H, CH$_3$)</td>
</tr>
<tr>
<td>IIlh</td>
<td>12.15 (s, 1H, NH), 8.74—8.89 (m, 4H, H-2, H-9, H-15), 7.84—8.06 (m, 5H, $H_{aron}$)</td>
</tr>
<tr>
<td>IVa</td>
<td>10.4 (br, 1H, OH-2'), 9.64 (s, 1H, H-5), 9.02 (br, 1H, NOH), 7.79 (d, 1H, H-6'), 7.49 (dd, 1H, H-4', $J_{e,k} = 2.1$ Hz, $J_{e,k} = 8.4$ Hz), 7.37 (s, 1H, H-3), 7.29 (d, 1H, H-3'), 2.40 (s, 3H, CH$_3$)</td>
</tr>
<tr>
<td>IVb</td>
<td>10.48 (br, 1H, OH-2'), 9.89 (br, 1H, OH-5'), 9.65 (s, 1H, H-5), 8.92 (br, 1H, NOH), 7.36 (s, 1H, H-3), 7.33 (d, 1H, H-6'), 7.27 (d, 1H, H-3'), 7.09 (dd, 1H, H-4', $J_{e,k} = 3.0$ Hz, $J_{e,k} = 7.9$ Hz)</td>
</tr>
</tbody>
</table>

Compounds IIle, IIlg, IIlh were measured on Tesla BS 487 A instrument (80 Hz) in DMSO. Compounds IVa, IVb were measured on Varian VXR-300 apparatus in DMSO.

The structure of prepared isoxazole derivatives was confirmed by $^1$H NMR spectra (Table 2). The IR spectra of $N$-(2-hydroxybenzoyl)-hydrazones (IIla, IIle, IIlkg, IIlh) indicated strong band at $\tilde{\nu} = 1617—1620$ cm$^{-1}$ for carbonyl group of pyrone, band at $\tilde{\nu} = 1641—1653$ cm$^{-1}$ of v(CO) amide and broad band centred at $\tilde{\nu} = 3153—3251$ cm$^{-1}$ of v(NH) and v(OH) groups. The other derivatives of III possess the similar IR values.

The $^1$H NMR spectra of $N$-(2-hydroxybenzoyl)-hydrazone (IIle) showed a singlet signal at $\delta = 8.80$ of H-2 and a singlet signal at $\delta = 8.63$ of H-9. Also the $^1$H NMR spectra of hydrazones IIlg, IIlh showed multiplet signals at $\delta = 8.65—8.89$ of H-2, H-9, and H-15.

In our study we found that the reaction between equimolar quantities of hydrazones IIlg or IIlm and hydroxylammonium chloride in pyridine gave derivatives of isoxazole IVa and IVb after removal of the hydrazide group (Formula 1).

$$\begin{array}{c}
\text{OH} \\
\text{N} \\
\text{OH} \\
\text{CH}_3 \\
\text{C} \\
\text{H}_3 \\
\text{R} \\
\text{R} \\
\text{NOH} \\
\text{IV} \\
\text{a} \quad \text{R} = \text{CH}_3-5' \\
\text{b} \quad \text{R} = \text{OH}-5' \\
\text{Formula 1} \\
\end{array}$$

The experimental method for testing on typical and atypical mycobacteria was used according to the published method [9].

3-Formylchromone $N$-Aroyl- or $N$-Alkyl-carbonylhydrazones Illa—IIlp

To solutions of 3-formylchromones (0.01 mol) in least amount of ethanol, solution of hydrazide derivatives (0.01 mol) in least amount of ethanol and one crystal of toluene-p-sulfonic acid were added. The mixture was stirred at temperature 50—60 °C for 30 min, filtered off, and the solid produced was boiled in ethanol, filtered off on hot to give Illa—IIlp (Tables 1 and 2).

4-[2-Hydroxyaryl]hydroxyiminomethyl]-isoxazoles (IVA, IVb)

A mixture of IIlg, IIlf or IIIk (0.022 mol) in pyridine (3 cm$^3$) and hydroxylammonium chloride (0.15 g; 0.22 mol) in water (1 cm$^3$) was refluxed for 4 h. The cooled mixture was poured over crushed ice and acidified with acetic acid and the solid that separated, was filtered off and recrystallized from cyclohexane or dioxane.

Acknowledgements. The authors are indebted to Ing. E. Greipllová for elemental analysis, Dr. A. Perjéssy, DrSc. for IR spectral measurements, and Dr. Matulová for $^1$H NMR measurements.

REFERENCES

Preparation and Pesticide Properties of Some 1-Substituted \(1H\)-1,2,4-Triazoles

S. STANKOVSKÝ, K. ŠPIRKOVÁ, E. JEDLOVSKÁ, and V. KONEČNÝ

Department of Organic Chemistry, Faculty of Chemical Technology, Slovak Technical University, SK-812 37 Bratislava
Research Institute of Chemical Technology, SK-831 06 Bratislava

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The preparation, infrared and \(^1H\) NMR spectra of five types of substituted 1-imidoyl-(1H)-1,2,4-triazoles are described. Herbicidal, fungicidal, and growth-regulating properties, tested on selected plants, are given.

So far, numerous pesticidally active compounds possessing the 1-substituted \(1H\)-1,2,4-triazole ring system have been prepared, and commercialized [1]. Triazoles with an imidoyl moiety have recently been added to this family of compounds (Formulas 1 and 2). Some diarylformamidinoyltriazoles [2] have been found to possess good fungicidal and nematocidal activity (type II, Formula 1), structures containing sulfonamide group were good herbicides [3], \(S\)-benzoylthiourea-substituted derivatives (type V, Formula 2) displayed bactericidal and fungicidal properties [4].

In our effort to enlarge the family of 1-substituted \((1H)\)-1,2,4-triazoles we described the synthesis and biological properties of some azolylquinazolines [5], in which the imidoyl moiety was built in the pyrimidine ring. Now we describe another five types of imidoyltriazoles, namely four \(N\)-phenylbenzimidoyltriazoles \(Ia\)–\(Id\), nine \(N\)-phenylformamidinoyltriazoles \(IIa\)–\(IIIi\), and four bis-triazolyl derivatives, formally guanidines \(IIia\)–\(IIIId\). Compounds \(IVa\), \(IVb\) are derivatives of \(O\)-methylthiourea, \(Va\), \(Vb\) can be classified as \(N\)-phenylhydroxamoyltriazoles.