
Mohamed A. Alkhader, Robert K. Smalley* (in part) Bagher Mohajerani

The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT, England

Indazole[2,1-g]indazole-6,12-diones 4 have been reported in the early literature as products from a variety of reactions including the thermal rearrangement of Heller's erroneously formulated 'bisanthraniil'. The correct structure of this 'bisanthraniil', which was obtained originally by the action of acetic anhydride on hydrazobenzene-2,2'-dicarboxylic acid, was elucidated by Mosby, and later confirmed by Gibson and Lindsay, as being the indazole[2,3-a][3,1]benzoxazin-5-one 3a. This heterocyclic system shows

a characteristic lactone νC=O band at 1780 cm⁻¹ and on heating in the solid state, or better in acetic anhydride, rearranges slowly to the isomeric indazolindazoledione 4a in quantitative yield.

As a potentially useful new route to the indazolobenzoxazines and hence, by rearrangement, the indazolindazolediones, we have investigated the cyclisation of 2-(6-nitrophenyl)- and 2-(6-nitrophenyl)-3,1-benzoxazin-4-ones 1a-m (Table 1), which are readily available in near quantitative yield by the action of either 6-nitrobenzoyl chloride or 6-nitrobenzoyl chloride on antranilic acid in pyridine solution. Thermolysis of the 6-nitrophenylbenzoxazines (1b, d, f, h-k, and m) in boiling 6-chlorobenzene is complete in 5-10 min and gives exclusively the indazolobenzoxazines 3a-h (Table 2). In contrast, the 6-nitrophenyl derivatives (1a, c, e, g, and l) with triethyl phosphate in boiling xylene (12-15 h) yield only the indazolindazolediones 4a-g (Table 3).

Formation of the pure indazolobenzoxazines is surprising in view of the reported thermal instability of these systems. However, we find that rearrangement of 3a→4a in boiling 6-chlorobenzene is very slow, only 10% rearranged product being formed after 48 h. Closer investigation of the triethyl phosphate reaction reveals that it too proceeds via the indazolobenzoxazine and that reaction is complete (as monitored by T.L.C. and I.R.) in about 3 h. On further heating, however, the indazolindazoledione begins to form as witnessed by the gradual disappearance of the lactone carbonyl band at 1780 cm⁻¹ and the appearance of the amide carbonyl band at 1700 cm⁻¹. Obviously the rearrangement of 3a→4a is aided by triethyl phosphate. In fact, we find that the phosphate ester is a superior reagent to acetic anhydride for promoting these rearrangements.

These cyclisations provide a general and selective method of synthesising the isomeric heterocycles 3 and 4, only a few examples of which have been reported previously. The chloro-derivatives (3e, f, and 4b), for example, have been identified only recently as the major products from the action of phosphorus pentachloride on azobenzene-2,2'-di-
carboxylic acid, a reaction reported originally by Freund-
ler. The method has been extended to the synthesis of the
benzindazoloindazoledione 7 and the indazolophthoxa-
zinone 6 from the (o-nitrophenyl)- and (o-azidophenyl)-
naphthoxaziones (5; Ar = o-\text{O}_2\text{NCH}_3 and o-N_2\text{C}_6\text{H}_5, re-
spectively).

\[
\begin{align*}
5 & \quad 6 \\
7 & 
\end{align*}
\]

Presumably, both reactions involve generation of the same
electrophilic nitrene species 2 which cyclises on to the adja-
cent nucleophilic nitrogen centre of the benzoxazine ring
as shown in the Scheme. Similar cyclisations of aryl azides
and o-nitroarenes are well-documented.

\[
\begin{align*}
\text{o-Azidobenzoic acid, o-azidobenzyl chloride, 3-chloroanthranilic}
& \text{acid, 3-chloro- and 5-chloro-2-azidobenzoic acid and their acid}
& \text{chlorides were prepared by the methods reported previously, as}
& \text{were 2-nitro- and 2-amino-5-acetamidobenzoic acid, and the 2-}
& \text{(o-nitrophenyl)- and 2-(o-azidophenyl)-3,1-benzoxazin-4-ones}
& \text{listed in Table 1.}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Product No.</th>
<th>(R^1)</th>
<th>(R^2)</th>
<th>(R^3)</th>
<th>(R^4)</th>
<th>(X)</th>
<th>Yield [%]</th>
<th>m.p. [°C]</th>
<th>Molecular formula</th>
<th>I.R. (nujol) [cm(^{-1})]</th>
<th>(\nu_{\text{C-O}})</th>
<th>(\nu_{\text{C-N}})</th>
<th>(\nu_{\text{N}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>NO(_2)</td>
<td>87</td>
<td>194</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1765</td>
<td>1625</td>
<td>1530; 1340</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>N(_3)</td>
<td>90</td>
<td>132</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1780</td>
<td>1620</td>
<td>2140; 2100</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>NO(_2)</td>
<td>91</td>
<td>144</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1780</td>
<td>1625</td>
<td>1530; 1350</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>N(_3)</td>
<td>88</td>
<td>132</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1780</td>
<td>1620</td>
<td>2150; 2100</td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>NO(_2)</td>
<td>88</td>
<td>207</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1765</td>
<td>1645</td>
<td>1520; 1345</td>
<td></td>
</tr>
<tr>
<td>1f</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>N(_3)</td>
<td>89</td>
<td>119</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1770</td>
<td>1630</td>
<td>2150; 2100</td>
<td></td>
</tr>
<tr>
<td>1g</td>
<td>Cl</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>NO(_2)</td>
<td>88</td>
<td>210</td>
<td>C(_9)H(_8)Cl(_2)N(_2)O(_4)</td>
<td>1770</td>
<td>1625</td>
<td>1525; 1345</td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>Cl</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>N(_3)</td>
<td>92</td>
<td>137</td>
<td>C(_9)H(_8)Cl(_2)N(_2)O(_2)</td>
<td>1775</td>
<td>1620</td>
<td>2150; 2100</td>
<td></td>
</tr>
<tr>
<td>1i</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>N(_3)</td>
<td>79</td>
<td>138</td>
<td>C(_9)H(_8)Cl(_2)N(_2)O(_2)</td>
<td>1770</td>
<td>1630</td>
<td>2145; 2100</td>
<td></td>
</tr>
<tr>
<td>1j</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>N(_3)</td>
<td>85</td>
<td>133</td>
<td>C(_9)H(_8)Cl(_2)N(_2)O(_2)</td>
<td>1770</td>
<td>1638</td>
<td>2120</td>
<td></td>
</tr>
<tr>
<td>1k</td>
<td>H</td>
<td>NO(_2)</td>
<td>H</td>
<td>H</td>
<td>N(_3)</td>
<td>62</td>
<td>138</td>
<td>C(_9)H(_8)NO(_2)</td>
<td>1760</td>
<td>1630</td>
<td>2130</td>
<td></td>
</tr>
<tr>
<td>1l</td>
<td>NHAc</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>NO(_2)</td>
<td>87</td>
<td>235</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1750</td>
<td>1630</td>
<td>1520; 1330</td>
<td></td>
</tr>
<tr>
<td>1m</td>
<td>NHAc</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>N(_3)</td>
<td>90</td>
<td>260</td>
<td>C(_9)H(_8)N(_2)O(_2)</td>
<td>1740</td>
<td>1700</td>
<td>2140; 2100</td>
<td></td>
</tr>
</tbody>
</table>

* The microanalyses were in satisfactory agreement with the calculated values (C ± 0.30, H ± 0.24, N ± 0.38).
Table 2. Indazolo[2,3-a][3,1]benzoxazin-5-ones 3

<table>
<thead>
<tr>
<th>Product**</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>R4</th>
<th>Yield [%]</th>
<th>m.p. [°C]</th>
<th>Molecular formulaa or Lit. m.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>85</td>
<td>183</td>
<td>C9H7ClN2O2 (270.7)</td>
</tr>
<tr>
<td>3b</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>81</td>
<td>206</td>
<td>C10H7ClN2O2 (270.7)</td>
</tr>
<tr>
<td>3c</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>83</td>
<td>230</td>
<td>C10H7ClN2O2 (305.1)</td>
</tr>
<tr>
<td>3d</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>82</td>
<td>221</td>
<td>C10H7Cl2N2O2 (305.1)</td>
</tr>
<tr>
<td>3e</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>83</td>
<td>240</td>
<td>239°</td>
</tr>
<tr>
<td>3f</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>Cl</td>
<td>74</td>
<td>209</td>
<td>210°</td>
</tr>
<tr>
<td>3g</td>
<td>H</td>
<td>NO2</td>
<td>H</td>
<td>H</td>
<td>87</td>
<td>248</td>
<td>C10H7N2O4 (281.2)</td>
</tr>
<tr>
<td>3h</td>
<td>NHAc</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>90</td>
<td>280</td>
<td>C10H7N2O4 (293.3)</td>
</tr>
</tbody>
</table>

* All the compounds exhibited a broad amide carbonyl band at 1700 cm⁻¹ (Nujol).

** The microanalyses were in satisfactory agreement with the calculated values (C ± 0.23, H ± 0.29, N ± 0.05); exception 3b: C – 0.51, N – 0.55.

Table 3. Indazolo[2,1-a]indazolo-6,12-diones 4

<table>
<thead>
<tr>
<th>Product**</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>Yield [%]</th>
<th>m.p. [°C]</th>
<th>Molecular formulaa or Lit. m.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>87</td>
<td>297</td>
<td>302°</td>
</tr>
<tr>
<td>4b</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>90°</td>
<td>231</td>
<td>222°</td>
</tr>
<tr>
<td>4c</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>89</td>
<td>244</td>
<td>C10H7ClN2O2 (270.7)</td>
</tr>
<tr>
<td>4d</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>70</td>
<td>228</td>
<td>195°</td>
</tr>
<tr>
<td>4e</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>91°</td>
<td>194</td>
<td>C10H7N2O4 (281.2)</td>
</tr>
<tr>
<td>4f</td>
<td>NO2</td>
<td>H</td>
<td>H</td>
<td>93°</td>
<td>246</td>
<td>C10H7N2O4 (293.3)</td>
</tr>
<tr>
<td>4g</td>
<td>NHAc</td>
<td>H</td>
<td>H</td>
<td>82</td>
<td>320</td>
<td></td>
</tr>
</tbody>
</table>

* All the compounds exhibited a broad amide carbonyl band at 1700 cm⁻¹ (Nujol).

** The microanalyses were in satisfactory agreement with the calculated values (C ± 0.23, H ± 0.10, N ± 0.21).

† Obtained by rearrangement of either 3b or 3f.

‡ Prepared by rearrangement of 3e.

§ Obtained by heating 3g with acetic anhydride.

Deoxygenation of 2-(o-Nitrophenoxy)-3,1-benzoxazin-4-ones 1: General Procedure:
The 2-(o-nitrophenoxy)-3,1-benzoxazin-4-one (1 g) in a mixture of triethyl phosphate (10 ml) and xylene (45 ml) is heated under reflux for 15-20 h. The resulting solution is then cooled in an ice/water bath in order to precipitate the product, or the solution is evaporated to dryness. In each case the solid product is washed with petroleum ether (b.p. 40-60 °C), dried, and reprecipitated from ethyl acetate as either colourless or pale yellow needles. Data are given in Table 3.

2-(o-Nitrophenoxy)naphtho[2,3-a][3,1]oxazin-4-one under the above conditions gives a mixture of 6 and 7 which can be separated by chromatography on a silica column (toluene as eluent). Alternatively, the mixture on prolonged heating with acetic anhydride or triethyl phosphate gives benzo[5,6]indazolo[2,1-a]indazolo-6,14-dione (7) as the sole product; yield: 87%; needles from ethyl acetate; m.p. 290 °C.

C15H14N2O2 calc. C 75.51 H 3.52 N 9.78
(286.3) found 75.50 3.58 9.79

I.R. (Nujol): ν= 1700 cm⁻¹ (C=O).

Rearrangement of Indazolo[2,3-a][3,1]benzoxazin-5-ones 3 to Indazolo[2,1-a]indazolo-6,12-diones 4: General Procedure:
Method A: The indazolo[2,3-a][3,1]benzoxazinone (0.5 g) is heated under reflux with acetic anhydride (30 ml) for 48-72 h. In most cases cooling the reaction mixture brings about precipitation of the indazoloindazoledione in quantitative yield. Alternatively the reaction mixture is evaporated to dryness and the solid residue crystallised from ethyl acetate. The products are identical (superimposable I.R. spectra and non-depressed mixture m.p.) with the products obtained by triethyl phosphate deoxygenation of the 2-(o-nitrophenoxy)-benzoxazin-4-ones (1; X = NO2).

With the exception of the nitrobenzoxazinone 3g, the rearrangements are also achieved by heating the indazoloindazoloazinones (0.5 g) with triethyl phosphate (8 ml) in boiling xylene (15 ml) for 15-16 h. Work-up, as in Method A yields the indazoloindazolediones in quantitative yield.

We thank the British Council for a postgraduate research award to M.A.A.

Received: December 7, 1979

Errata and Addenda 1980

V. N. R. Pillai, Synthesis 1980 (1), 1-26;
The structure of compound 86 (p. 12) should be:

\[
\text{R}^1 - \text{N} - \text{R}^2
\]

V. I. Cohen, Synthesis 1980 (1), 60-63;
The alternative name (in brackets) for compounds 1 (p. 62, first experimental procedure) should be \(S\)-Methylpseudothiohyra Hydroiodides.

J. R. Mahajan, H. C. de Araujo, Synthesis 1980 (1), 64-66;
The authors have erroneously stated that “exaltolide” is a trivial name for pentadecanolide. In fact “exaltolide” is a trademark registered in the name of Firmenich SA, Geneva and should be designated as Exaltolide.”

V. I. Gorbatenko, L. I. Samarai, Synthesis 1980 (2), 85-110;
The structure of compound 97 (p. 99) should be:

\[
\begin{array}{c}
\text{Ar} \\
\text{R} - \text{C} - \text{NH} - \text{C}
\end{array}
\]

M. Mikołajczyk, P. Balczewski, S. Grejuszczak, Synthesis 1980 (2), 127-129;
The correct name for compound 5a (first procedure, p. 129) is Diethyl 1-Phenylthiocarbamoylphosphonate.

The correct name for compound 4 is \(N\)-(Chlorosulfonyl)-dimethylsulfilimine.

Abstract 5692, Synthesis 1980 (2), 159;
The title should be: \textit{Phenols from Aryl Ethyl Ethers}.

Abstract 5698, Synthesis 1980 (2) 161;
The title should be: \textit{Enals and Enones from Ketones}.

The structures of compounds 90 (p. 175) should be:

\[
\begin{array}{c}
\text{X} \\
\text{R} - \text{O} - \text{N}
\end{array}
\]

The correct name for compound 251 (p. 188) is \(2H\)-Cycloheptadipyrrolizin-Derivat.

Abstract 5724, Synthesis 1980 (3), 254;
The title should be: \textit{Carbamates, Thio Carbamates, and Carbonates from Alcohols or Thiols}.
The first line under the formula scheme should be: \(Y = O, S\).

Abstract 5728, Synthesis 1980 (3), 256;
The title (and name for compound 3) should be: \(N\)-Sulphenylimines Derived from Amino Acids.

C. R. Harrison, P. Hodge, Synthesis 1980 (4), 299-301;
The 3rd group in the Table, part B (p. 300) should have the structure:

\[
\begin{array}{c}
\text{H}_2\text{C} \\
\text{H}_2\text{C} - \text{N} - \text{C} - \text{C}_2\text{H}_5
\end{array}
\]

Abstract 5745, Synthesis 1980 (4), 334;
The title should be: \textit{Stereocontrolled cis-Addition of Organocopper Reagents to 2-Alkynals, 1-Alkynyl Ketones, 2-Alkynoic Acids, and 2-Alkynoic Esters}.

Abstract 5752, Synthesis 1980 (6), 336;
The title should be: \textit{\(\alpha\)-Alkylation and \(\alpha\)-Alkyldenation of Carbonyl Compounds}.
The formula scheme for the conversion 3 \(\rightarrow\) 4 or 5 should be:

\[
\begin{align*}
\text{NaX} & + \text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{CCl}_4, \nu \rightarrow 81 - 97\% \\
\text{R}^1 + \text{H} & \rightarrow \text{R}^2 \text{C}_6\text{H}_5 \\
\text{W} + \text{2}{\text{Hexane Ni} / 3:1} \\
\text{acetic acid / ethanol, 21.} & \rightarrow 95 - 98\%
\end{align*}
\]

Abstract 5770, Synthesis 1980 (4), 342;
The title should be: \textit{Claisen Rearrangement of Ketene Allyl Ethyl Acetals}.

The correct name for compound 6 is \textit{Indazolo[3,2-b][naphtho[2,3-d]-[1,3] oxazin-6-one}.

Abstract 5782, Synthesis 1980 (5), 418;
The formula scheme should be:

\[
\begin{align*}
\text{R}^1\text{CO} & + 3 (\text{C}_2\text{H}_3)_2\text{P} = \text{CH} - \text{R}^3 \\
\text{Method A} & \rightarrow 93 - 96\%
\end{align*}
\]

Abstract 5799, Synthesis 1980 (5), 434;
The structures of compounds 2 and 3 should be:

\[
\begin{array}{c}
\text{H}_2\text{C} - \text{S} - \text{CH} = \text{CH} - \text{S} - \text{CH}_2 \\
\text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \quad \text{R}^4
\end{array}
\]

L. M. Harwood, M. Julia, Synthesis 1980 (6), 456-457;
The structure of compound (-)-7 should be:

\[
\text{(-)-7}
\]

T. Sasaki, S. Eguchi, T. Okano, Synthesis 1980 (6), 472-475;
The structure of compound 5 should be:

\[
\begin{align*}
\text{O} \quad \text{NH} - \text{C} - \text{OC}_2\text{H}_5 \\
\text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \\
\end{align*}
\]

Abstract 5804, Synthesis 1980 (6), 498;
The title should be: \textit{Allylic Funcionisation of Exomethylene Compounds}.

Abstract 5817, Synthesis 1980 (6), 503;
The structure of compound 5 should be:

\[
\begin{align*}
\text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \quad \text{S} - \text{C}_6\text{H}_5 \\
\end{align*}
\]