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## Formation of 2-Aryl-4-benzoyl-2-methyl-5-phenyl-2*H*-imidazole

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The reaction of 3a-aryl-5, 6a-diphenyl-3a, 6a-dihydro-2*H*-furo [3, 2-*b*] pyrrole-2, 6 (3*H*) -diones (**1**) with aqueous ammonia produced 2-aryl-4-benzoyl-2-methyl-5-phenyl-2*H*-imidazoles (**2**). The molecular structures of **2** were determined by means of an X-ray crystal structure of the *p*-tolyl derivative **2b**.

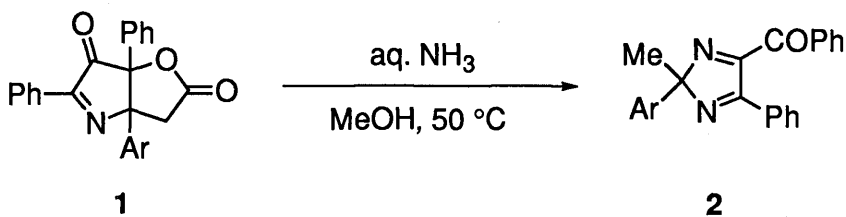
### Introduction

We previously reported that 3a, 5, 6a-triaryl-3a, 6a-dihydro-2*H*-furo [3,2-*b*] pyrrole-2, 6 (3*H*) -diones (**1**) are transformed into polysubstituted pyrrole derivatives by the reaction with various amines.<sup>1)</sup> The above transformations are considered to be initiated by the lactone ring-opening of **1** and to proceed via the cleavage of the central C (3a)-C (6a) bond.

Here we describe our findings that the treatment of **1** with aqueous ammonia, the most fundamental amine, causes the fission of the central C (3a)-C (6a) bond, giving 2*H*-imidazole **2**.

### Results and Discussion

A mixture of **1a** and 28% aqueous ammonia in methanol was heated at 50 °C for 3h, giving a dark reaction mixture. From the mixture, a colorless crystalline product **2a** was isolated in 31% yield by means of column chromatography on silica gel (**Scheme 1**).



**a: Ar=Ph, b: Ar=p-MeC<sub>6</sub>H<sub>4</sub>, c: Ar=p-ClC<sub>6</sub>H<sub>4</sub>**

**Scheme 1**

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Similarly **2b** and **2c** were obtained in 8% and 23% yields, respectively.

From the elemental analyses and spectral data, it was deduced that **2** might be either an imidazole or a pyrazole derivative with aryl, benzoyl, methyl, and phenyl groups as substituents. Further clarification of the structure of **2** on the basis of its spectral data seemed difficult, because of the many isomeric structures possible. Fortunately, **2b** gave a suitable crystal for the X-ray crystallographic analysis from light petroleum (40–60 °C) and the structure of **2** was established as 2-aryl-4-benzoyl-2-methyl-5-phenyl-2*H*-imidazole. This is the first example of an X-ray crystallographic analysis of 2*H*-imidazole derivatives, to the best of our knowledge.

The ORTEP drawing of **2b** is shown in Fig. 1. Bond distances and bond angles are given in Table 1 and 2. The 2*H*-imidazole ring of **2b** is almost planar. The dihedral angle between the C(8)–C(10)–C(11) and N(1)–C(10)–C(11) planes is 1.08° and that between C(8)–C(10)–C(11) and C(8)–N(1)–N(2) planes is 2.31°. The ring forms an irregular pentagon. The bond distances of two C–N bonds N(1)–C(8) and N(2)–C(8) are 1.42 and 1.52 Å, respectively. The bond angle of N(1)–C(10)–C(11) is 107° and that of N(2)–C(11)–C(10) is 111°. The bond distances of the two C=N bonds (N(1)=C(10) and N(2)=C(11) are 1.27 and 1.28 Å, respectively) are almost equal to the typical length of a C=N bond linked to an sp<sup>2</sup>-hybridized atom (1.27 Å)<sup>21</sup> and are shorter than those of a 1*H*-imidazole ring (1.37 Å and 1.38 Å)<sup>21</sup>. The C(10)–C(11) bond length is 1.53 Å,

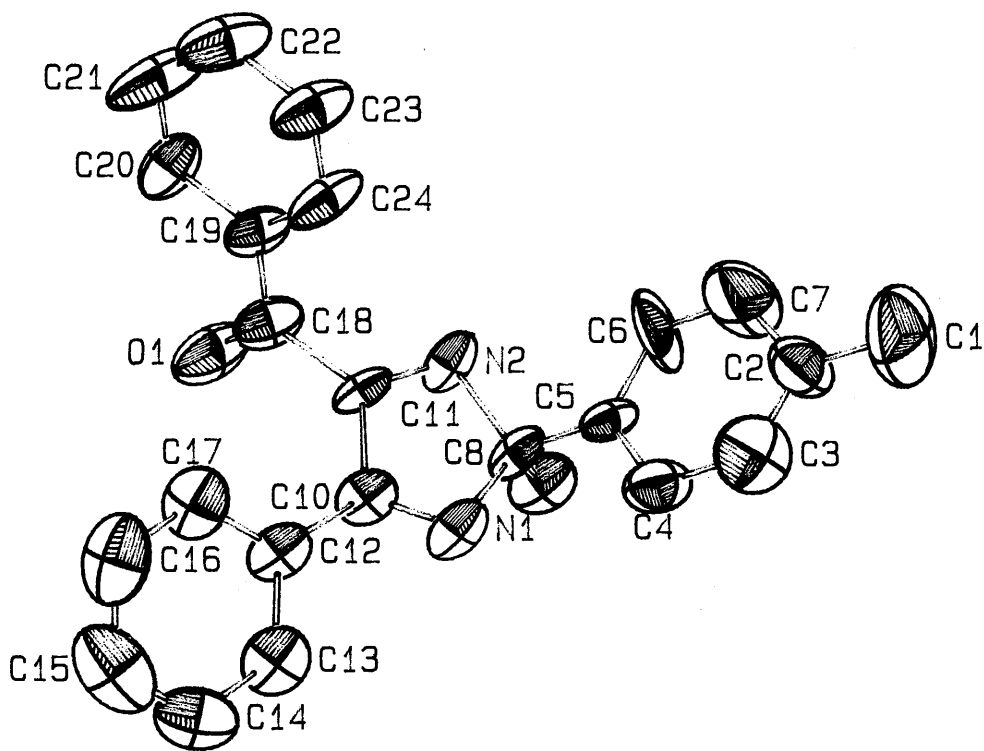


Fig. 1 ORTEP Drawing of **2b**.

**Table 1** Bond Distances of **2b** in Angstroms.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O1	C18	1.20(1)	C10	C12	1.45(1)
N1	C8	1.42(1)	C11	C18	1.54(1)
N1	C10	1.27(1)	C12	C13	1.40(1)
N2	C8	1.52(1)	C12	C17	1.40(1)
N2	C11	1.28(1)	C13	C14	1.35(1)
C1	C2	1.40(1)	C14	C15	1.35(2)
C2	C3	1.27(1)	C15	C16	1.36(1)
C2	C7	1.45(2)	C16	C17	1.33(1)
C3	C4	1.37(1)	C18	C19	1.45(1)
C4	C5	1.42(1)	C19	C20	1.44(1)
C5	C6	1.34(1)	C19	C24	1.41(1)
C5	C8	1.47(1)	C20	C21	1.34(2)
C6	C7	1.30(1)	C21	C22	1.38(1)
C8	C9	1.54(1)	C22	C23	1.41(1)
C10	C11	1.53(1)	C23	C24	1.33(1)

Numbers in parenthesis are estimated standard deviations in the least significant digits.

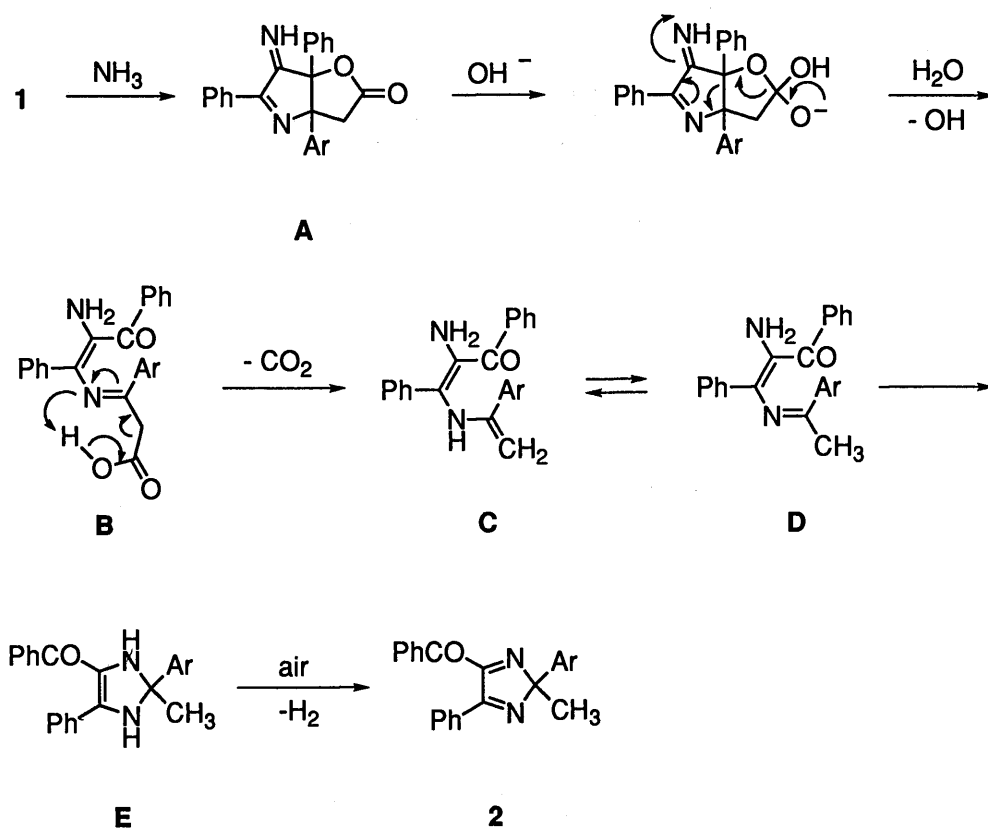
**Table 2** Bond Angles of **2b** in Degree.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C8	N1	C10	100.2(7)	N2	C11	C18	121.5(7)
C8	N2	C11	103.7(6)	C10	C11	C18	127.1(7)
C1	C2	C3	126 (1)	C10	C12	C13	120.0(8)
C1	C2	C7	122.4(9)	C10	C12	C17	123.6(8)
C3	C2	C7	111.3(9)	C13	C12	C17	116.3(8)
C2	C3	C4	130 (1)	C12	C13	C14	122.1(9)
C3	C4	C5	117.3(8)	C13	C14	C15	119.7(9)
C4	C5	C6	114.0(8)	C14	C15	C16	119.5(9)
C4	C5	C8	119.7(7)	C15	C16	C17	122 (1)
C6	C5	C8	126.2(8)	C12	C17	C16	120.4(9)
C5	C6	C7	126 (1)	O1	C18	C11	116.2(8)
C2	C7	C6	121.4(9)	O1	C18	C19	126.4(9)
N1	C8	N2	107.4(6)	C11	C18	C19	117.3(8)
N1	C8	C5	115.2(7)	C18	C19	C20	118.4(8)
N1	C8	C9	111.0(7)	C18	C19	C24	124.9(9)
N2	C8	C5	106.6(6)	C20	C19	C24	116.7(9)
N2	C8	C9	104.9(7)	C19	C20	C21	118.1(9)
C5	C8	C9	111.1(7)	C20	C21	C22	125 (1)
N1	C10	C11	107.1(7)	C21	C22	C23	117 (1)
N1	C10	C12	127.6(8)	C22	C23	C24	119.4(9)
C11	C10	C12	125.3(7)	C19	C24	C23	123.5(9)
N2	C11	C10	111.4(7)				

Numbers in parenthesis are estimated standard deviations in the least significant digits.

which is a typical value for a C(sp<sup>3</sup>)-C(sp<sup>3</sup>) single bond and is longer than a C-C bond of the 1*H*-imidazole ring (1.36 Å)<sup>2)</sup>. This means that conjugation between the two C=N units of **2b** is very small.

The formation pathway of **2** is tentatively proposed (**Scheme 2**). Reaction of **1** with ammonia forms imine intermediate **A**. Attack of hydroxide ion on the lactone-carbonyl group of **A** leads to the cleavage of the central C-C bond and the ring-opened intermediate **B** is produced. Due to a β-iminocarboxylic acid sub-unit, **B** eliminates carbon dioxide, giving **C**. Cyclization of the tautomer **D** affords the imidazoleine **E**, which is then oxidized by air to give 2*H*-imidazole **2**.



Scheme 2

### Experimental section

All of the melting points were determined on a Mitamuraiken MELT THERMO and are uncorrected. The IR spectra were measured as KBr pellets on a Nippon-Bunko IR-700. The MMR spectra were recorded at 270 MHz with a JEOL EX-270 in deuteriochloroform using TMS as an internal standard. The Mass spectra were obtained on a JEOL JMS-01SG-2

mass spectrometer at 75 eV using a direct inlet system. Column chromatography was carried out on silica gel (Wako gel, C-300)

**4-Benzoyl-2-methyl-2, 5-diphenyl-2H-imidazole (2a).** **Typical procedure.** A solution of **1** (500mg, 1.36mmol) and 28% -aqueous ammonia (5ml, 91mmol) in methanol (30ml) was heated at 60°C for 3h and then poured into water (100ml). The mixture was made acidic (pH 4) by dropwise addition of concentrated sulfuric acid and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (50ml×2). The extract was dried (MgSO<sub>4</sub>) and evaporated in vacuo to leave the residue which, on chromatography (benzene), gave **2a** (145mg, 31%): Colorless needles (hexane); mp 106-108°C; IR 3062, 2986, 2932, 1664cm<sup>-1</sup>; <sup>1</sup>H-NMR δ = 1.95 (3H, s), 7.20-7.80 (13H, m), 7.90-8.10 (2H, m); <sup>13</sup>C-NMR δ = 27.35, 107.44, 127.05, 127.87, 128.46, 128.58, 128.75, 128.87, 130.10, 130.69, 130.98, 130.74, 135.03, 139.61, 162.10, 162.91, 191.69; MS m/z 338 (M<sup>+</sup>), 233, 207, 105. Found: C, 81.68; H, 5.48; N, 8.26%. Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O: C, 81.63; H, 5.36; N, 8.28%.

**4-Benzoyl-2-methyl-5-phenyl-2-p-tolyl-2H-imidazole (2b).** A solution of **1b** (500 mg, 1.31mmol) and 28% -aqueous ammonia (5ml, 91mmol) in methanol (30ml) was heated at 50°C for 1.5h and worked up as described above, giving **2b** (37mg, 8%) as colorless prisms (light petroleum): Mp 81-83 °C; IR 2986, 2930, 1675cm<sup>-1</sup>; <sup>1</sup>H-NMR δ = 1.86 (3H, s), 2.27 (3H, s), 7.10-7.70 (12H, m), 7.94 (2H, d, J = 7 Hz); <sup>13</sup>C-NMR δ = 20.07, 26.24, 106.41, 125.96, 127.62, 127.74, 127.89, 128.17, 129.16, 129.81, 129.94, 133.73, 134.07, 135.63, 136.64, 161.04, 161.87, 190.78; MS m/z 352 (M<sup>+</sup>), 247, 221, and 105. Found: C, 81.52; H, 5.72; N, 8.02%. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O: C, 81.79; H, 5.72; N, 7.95%.

**4-Benzoyl-2-p-chlorophenyl-2-methyl-5-phenyl-2H-imidazole (2c).** A solution of **1c** (512mg, 1.27mmol) and 28% -aqueous ammonia (5ml, 91mmol) in methanol (30ml) was heated at 50°C for 3.5h and worked up as described above, giving **2c** (110mg, 23%): Colorless crystalline powder; mp 58-62°C; IR 3062, 2984, 2926, 1669cm<sup>-1</sup>; <sup>1</sup>H-NMR δ = 1.93 (3H, s), 7.18-7.78 (12H, m), 8.01 (2H, d, J = 7Hz); <sup>13</sup>C-NMR δ = 27.42, 106.99, 128.59, 128.66, 128.75, 128.82, 129.00, 130.17, 130.58, 131.23, 133.87, 134.91, 135.02, 138.24, 162.41, 163.27, 191.70; MS m/z 374 (M<sup>+</sup>), 372 (M<sup>+</sup>), 269, 267, 105. Found: C, 73.27; H, 4.85; N, 7.16%. Calcd for (C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>OCl + 0.25H<sub>2</sub>O): C, 73.20; H, 4.67; N, 7.42%.

**X-Ray crystal analysis of 2b. Crystallographic Section.** C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O, M<sub>w</sub> = 338.39, monoclinic, space group P2<sub>1</sub>/n, a = 9.673 (5), b = 20.281 (11), c = 10.275 (5) Å, α = 90.024 (42), β = 95.303 (41), γ = 90.055 (43)°, V = 2007.11 Å<sup>3</sup>, Z = 2, D<sub>x</sub> = 1.289 g·cm<sup>-3</sup>.

**Data Collection.** Diffractometer: CAD 4 (ENRAF-NONIUS), crystal size: 0.1×0.1×0.1mm, radiation: Ni-filtered Cu Kα (1.54184 Å), monochromator: data collecting mode: ω-2θ scan, number of reflectance: 1267 (observed), temperature: 298°K.

**Structure Analysis.** Solution: SIR, R = 0.0988, R<sub>w</sub> = 0.1079, software: MOLEN.

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