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`[E012]`

9H-Dibenzo[a,c]carbazole from microwave assisted Madelung's reaction of N-[2-(phenylmethyl)phenyl]benzamide

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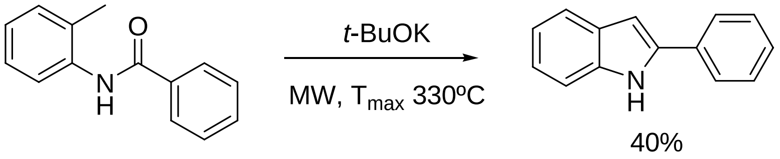
Abstract: Microwave irradiation of N-[2-(phenylmethyl)phenyl]benzamide with potassium tert-butoxide leads to a 1:1 ratio of the expected product from Madelung's reaction and 9H-Dibenzo[a,c]carbazole. This one seems to come from a competitive reaction pathway rather than from thermal conrotatory electrocyclic of 2,3-diphenyl-3H-Indole.

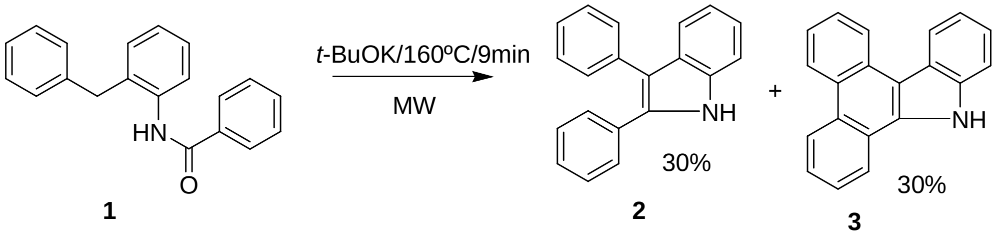
Madelung's synthesis of indole is one of the typical reactions to prepare this heterocycle. Classically, this synthesis is achieved treating *N*-benzoyl-*o*-toluidines with alkoxides at high temperatures (360-380ºC).

Our group has previously described the use of microwave irradiation to improve this reaction (Scheme 1)



Scheme 1

In order to check the influence of a phenyl group at the benzylic position where the anion is formed, N-[2-(phenylmethyl)phenyl]benzamide was prepared and irradiated in a multimode microwave oven at 160ºC for 9 minutes. The disappearance of the starting material was accompanied with the appearance of two compounds, which after isolation resulted in the expected 2,3-diphenyl-3H-Indole (30% yield) and 9H-dibenzo[a,c]carbazole (30% yield). Scheme 2.



Scheme 2

The structure of unexpected compound **3** was established by its spectral properties. ^{1}H NMR of this compound is shown to be identical with the reported by Martín et al.[1] (Figure 1, respectively).

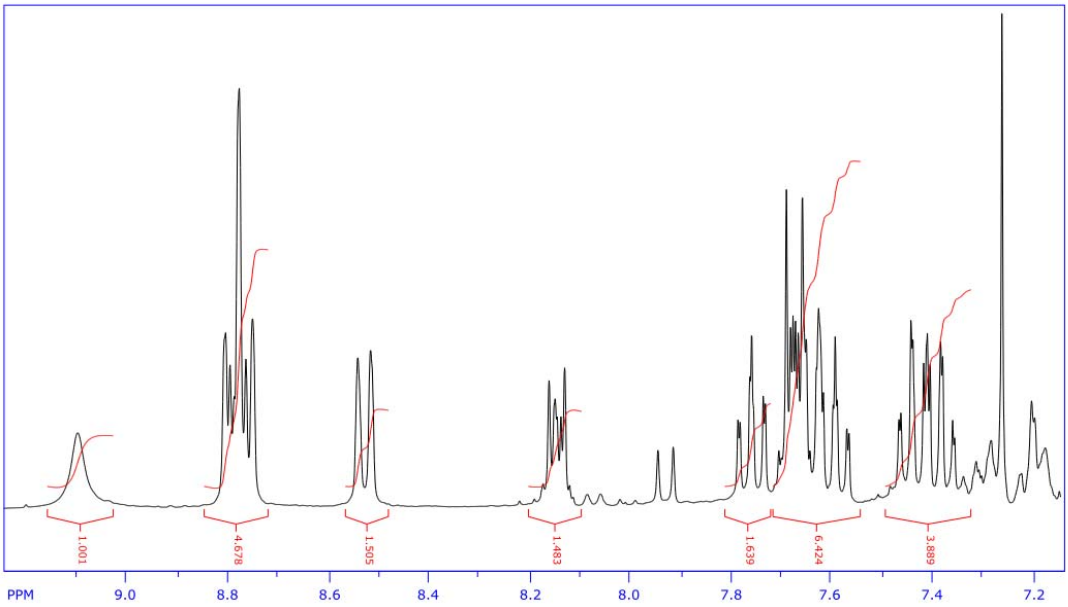
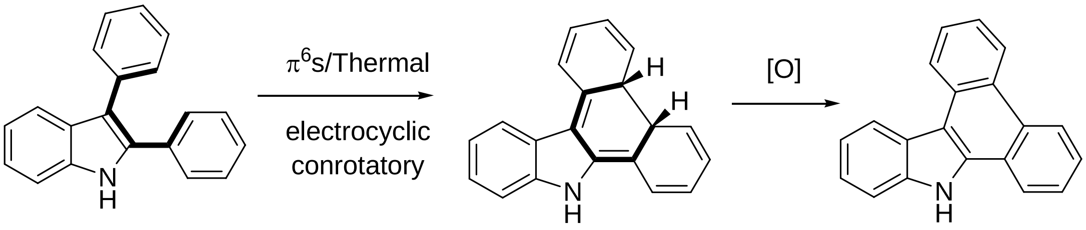


Figure 1. ^{1}H NMR of **3** obtained by microwave irradiation of **1**.

The formation of the dibenzocarbazole nucleus could be attributed to a thermal electrocyclic conrotatory cyclization (Scheme 3).



2

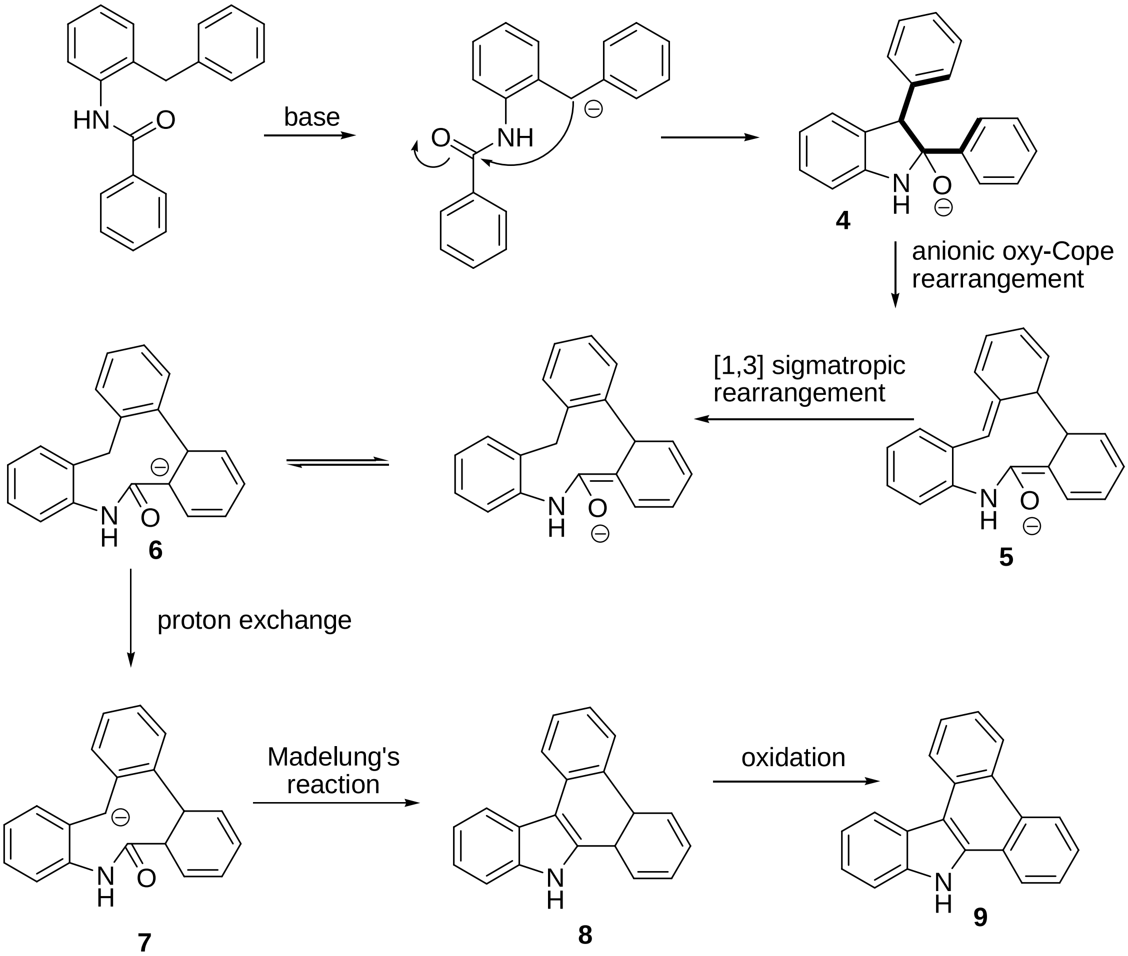
3

Scheme 3

However, when compound **2** was irradiated in the presence of potassium tert-butoxide under the same conditions as **1**, no dibenzocarbazole was detected.

Furthermore, the Scholl oxidation, which generates a new C−C bond between two unfunctionalized aryl positions, was discarded since it requires an oxidant and a strong acid.[2]

An alternative is a mechanism (scheme 4) through an anionic oxy-Cope rearrangement that would lead to the formation of the biaryl bond in intermediate **5**. This would rearrange to **6** which would give, after a proton migration, compound **7**. This one is the starting material for a second Madelung's reaction to yield dihydrobenzocarbazole **8**, which is expected to undergo easy oxidation with atmospheric oxygen to gain aromaticity.



Scheme 4

In summary, we report an unusual transformation from microwave assisted Madelung’s reaction to give 9H-Dibenzo[a,c]carbazole. It is proposed a cascade mechanism where an anionic oxyCope rearrangement, two Madelung’s condensations, a [1,3]-sigmatropic and oxidation steps are involved.

Acknowledgements

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Experimental Procedure

N-[2-(phenylmethyl)phenyl]benzamide (300 mg, 1.04 mmol) is thoroughly mixed with potassium *tert*-butoxide (293 mg, 2.61 mmol) were irradiated in a multimode microwave oven (Milestone Ethos D) for 9 minutes with a power of 1000W and maximum temperature settled at 160ºC. After disappearance of the starting material, the crude product was dissolved in dichloromethane (20 ml) and washed with 10% $NaOH_{aq}$ (20 mL), 10% HCl_{aq} (20 mL) and water (20 mL). Organic layer was dried with Na_2SO_4 anhydrous and evaporated. The residue was purified by chromatography (AcOEt/hexanes, 1:9) yielding diphenyl indol **2** (85 mg, 30%) and benzocarbazole **3** (83 mg, 30%).

2,3-diphenyl-3H-Indole (2). ^{1}H-RMN (300 MHz, $CDCl_3$), δ 8.23 (s_b, 1H, NH), 7.68 (d, J=7.91 Hz, 1H, ArH), 7.50-7.21 (m, 12H, ArH), 7.18-7.13 (m, 1H, ArH). ^{13}C-RMN (75 MHz, $CDCl_3$), δ 136.2, 135.3, 134.3, 133.0, 130.4, 129.1, 128.9, 128.7, 128.4, 127.9, 126.4, 122.9, 120.6, 119.9, 115.4, 111.0. MS m/z (%): 270 (M^++1, 22), 269 (M^+, 100), 268 (M, 14), 165 (11). IR υ_{max} (KBr, film): 3414 (NH), 2957, 2924, 1603, 1456, 1263, 742, 700 cm^{-1}.

9H-Dibenzo[a,c]carbazole (3). ^{1}H-RMN (300 MHz, $CDCl_3$), δ: 9.10 (br s, 1H, NH), 8.84-8.75 (m, 2H, ArH), 8.53 (d, J=7.66 Hz, 1H, Ar-H), 8.14 (dd, J=6.41, 2.91 Hz, 1H, Ar-H), 7.80-7.55 (m, 4H, ArH), 7.49-7.03 (m, 3H, ArH), 6.86-6.70 (m, 1H, ArH). ^{13}C-RMN (75 MHz, $CDCl_3$), δ: 129.5, 188.9, 127.5, 126.9, 126.4, 124.2, 124.1, 124.0, 123.9, 123.8, 122.0, 121.0, 120.9, 111.6, 101.4. MS m/z (%): 268 (M^++1, 28), 267 (M^+, 100), 266 (M, 15), 133 (13). IR υ_{max} (KBr, film): 3427 (N-H), 2959, 2924, 1745, 1610, 1462, 746 cm^{-1}.

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[1] M.E. Budén, V. A. Vaillard, S. E. Martin, R. A. Rossi. *J. Org. Chem.* **2009**, *74*, 4490–4498.

[2] B. T. King, J. Kroulík,, C. R. Robertson, P. Rempala,, C. L. Hilton, J. D. Korinek, L. M. Gortari. *J. Org. Chem.* **2007**, 72, 2279-2288.