

Steric control in the ion radical nitration of 5-triphenylmethylbenzimidazolines using a silver/nitrite system

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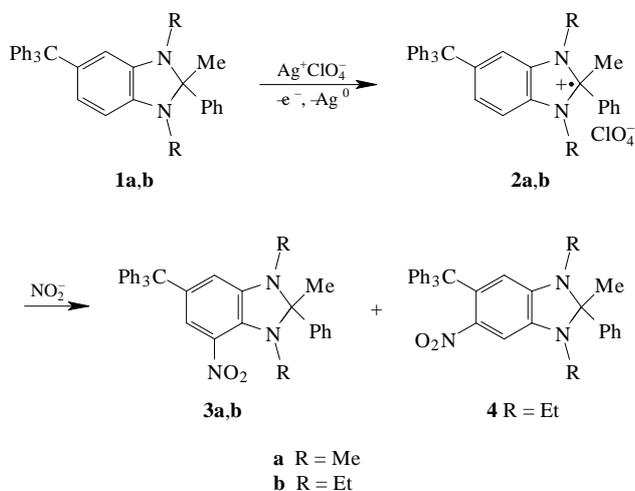
Nitration of 1,2,2,3-tetrasubstituted 5-triphenylmethylbenzimidazolines using an $\text{Ag}^+/\text{NO}_2^-$ system shows an unexpected (for benzimidazolines) orientation of the nitro group into position 7, which may be due to the strong steric influence of the rather bulky triphenylmethyl substituent.

1,2,2,3-Tetra- and 1,2,2,3,5-penta-substituted 2,3-dihydrobenzimidazoles (benzimidazolines) undergo fast nitration with mild one-electron oxidants and sodium nitrite to yield the corresponding 5-nitro- or (in the case of compounds with a Me, NO_2 or CHO group at position 5) 4- or 6-nitro-derivatives.¹ This process involves one-electron oxidation of benzimidazoline and subsequent attack of benzimidazoline radical cation (RC) by nitrite anion. The regioselectivity of the reaction is determined in this case by an electronic factor (electronic structure of RC).²

In this paper we demonstrate using benzimidazolines as an example that the steric factor may also play a decisive role in the orientation of the nitro group due to the ion radical nitration of substrates with rather bulky substituents. Such substituents may hinder the introduction of a nitro group to the neighbouring *o*-position due to their large size.

A typical situation involves nitration of 1,2,2,3-tetra-substituted 5-triphenylmethylbenzimidazolines using the $\text{AgClO}_4\text{-NaNO}_2$ system. This reaction was investigated for 1,2,3-trimethyl-2-phenyl- **1a** and 1,3-diethyl-2-methyl-2-phenyl-5-triphenylmethylbenzimidazoline **1b** (Scheme 1).[†] The nitration proceeds in acetonitrile and is initiated by rapid formation of green-coloured RC **2a,b**,³ which reacts in the next, much slower, stage with NO_2^- to yield red-coloured 7-nitro derivatives **3a,b**. The corresponding 6-nitroisomers may also be formed as by-products. The ion radical character of the reaction is confirmed by observation (EPR) or isolation of perchlorates of RC in systems containing 5-triphenylmethylbenzimidazolines and AgClO_4 ,³ as well as by preparation of nitrobenzimidazoline **3a** on interaction of salt **2a**⁺ ClO_4^- with NaNO_2 in acetonitrile.

This reaction is the first example of ion radical nitration to be controlled by steric factors.



Scheme 1

References

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[†] *Reaction procedure.* A suspension of benzimidazoline **1a**³ (0.58 g) and NaNO_2 (2 g) in acetonitrile (12 ml) was treated with a solution of $\text{AgClO}_4 \cdot 4\text{MeCN}$ ⁴ (0.39 g) in the same solvent (5 ml) with stirring during 6 h. After 10 min the reaction mixture became deep green and towards the end of the reaction, red. Nitro compound **3a** was precipitated by water, filtered off, dried and recrystallized from acetonitrile to give 0.46 g (73%) of **3a** as a red microcrystalline powder, mp 221–223 °C. Nitration of benzimidazoline **1b** was carried out similarly, but the reaction proceeds much more slowly (46 h). Nitro isomers **3b** and **4** were separated by column chromatography (Al_2O_3 , benzene). Yields of compounds **3b** and **4** were 44% and 5%, respectively. **3b**: mp 190–192 °C (MeCN); **4**: mp 119–122 °C (MeCN). All new compounds gave satisfactory elemental analyses.

¹H NMR (80 MHz); for **3a** (CDCl_3) δ : 1.74 (s, 3H, $\text{C}^2\text{-Me}$), 2.23 (s, 3H, $\text{N}^3\text{-Me}$), 2.60 (s, 3H, $\text{N}^1\text{-Me}$), 5.80 (d, 1H, $^4J = 1.6$ Hz, H^5), 6.95 (d, 1H, $^4J = 1.6$ Hz, H^6), 7.0–7.6 (m, 20H, 4Ph); for **3b** (CDCl_3) δ : 0.60 (t, 3H, $^3J = 6.9$ Hz, CH_2CH_3), 0.66 (t, 3H, $^3J = 6.8$ Hz, CH_2CH_3), 1.85 (c, 3H, $\text{C}^2\text{-Me}$), 2.74 (q, 2H, $^3J = 6.9$ Hz, $\text{N}^3\text{-C H}_2$), 3.23 (q, 2H, $^3J = 6.8$ Hz, $\text{N}^1\text{-C H}_2$), 5.72 (d, 1H, $^4J = 1.8$ Hz, H^5), 6.93 (d, 1H, $^4J = 1.8$ Hz, H^6), 7.1–7.6 (m, 20H, 4Ph); for **4** ($[\text{D}_6]\text{acetone}$) δ : 0.68 (t, 3H, $^3J = 7.0$ Hz, CH_2CH_3), 1.00 (t, 3H, $^3J = 7.1$ Hz, CH_2CH_3), 1.88 (s, 3H, $\text{C}^2\text{-Me}$), 2.8–3.1 (m, 4H, 2N-C H_2), 5.90 (s, 1H, H^5), 6.81 (s, 1H, H^6), 7.0–7.6 (m, 20H, 4Ph).