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# The first example of reversible C-azo coupling in a series of aromatic and heteroaromatic compounds

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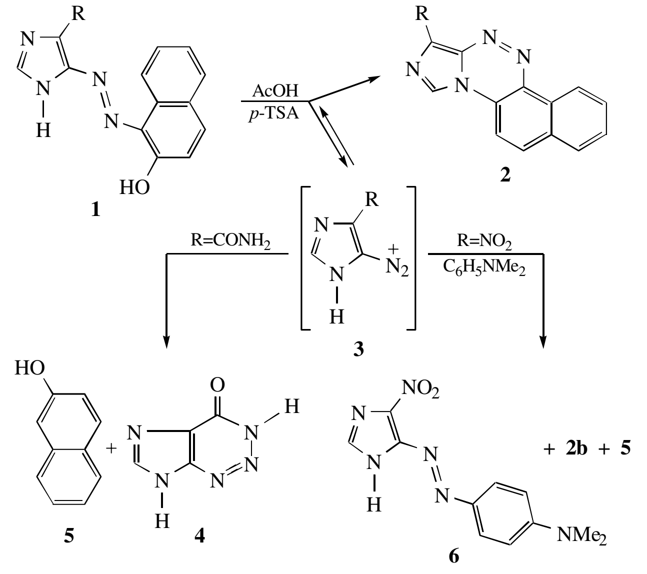
**Heating of imidazolyl- and phenylazo-naphthols in acetic acid in the presence of *p*-toluenesulfonic acid and dimethylaniline yields imidazolyl- and phenyl-(*p*-dimethylamino)azobenzenes, which suggests the intermediacy of the corresponding diazo compounds.**

It is well-known that azoamino compounds can undergo cleavage of the N–N bond under acidic conditions, thus being transformed into diazo compounds.[1,2] In addition, aryl and heteroaryl-formazans obtained from the interaction of aryldiazonium salts with hydrazones are unstable in acid media, and the formation of products in this reaction is explained by elimination of the diazonium salts.[3–5] On the other hand, no evidence for the reversibility of the C-azo coupling reaction in the series of 'classical' azo compounds has so far been described in the literature.

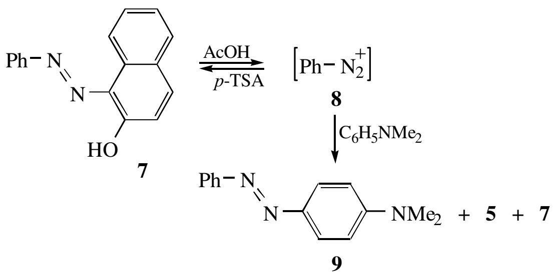


**1,3 a** R = $CONH_2$
**b** R = $NO_2$

**Scheme 1**

We have found that refluxing 1-(4-carboxamide-5-imidazoylazo)-2-naphthol **1a** in acetic acid in the presence of catalytic amounts of *p*-toluenesulfonic acid affords the expected carbamoylnaphthoimidazotriazine **2a**† together with unexpected imidazo-[4,5-*d*][1,2,3]triazin-4-one **4** and 2-naphthol **5**, isolated by column chromatography in the ratio 1:3 (by weight). Under these conditions, 5-diazoimidazole-4-carboxamide **3** is transformed irreversibly into imidazotriazine **4** (Scheme 1).

The formation of **4** from the azo compound **1a** can be rationalized as a result of the retro-azo coupling reaction. In this conversion the aminocarbonyl group in compound **1a** serves as an intramolecular trap for the diazo group. Further evidence for the formation of the intermediate diazo compound **3** was obtained by using an extrinsic trap, namely dimethylaniline, which was allowed to react with 1-(4-nitro-5-imidazolylazo)-2-naphthol **1b**. In addition to naphthoimidazotriazine **2b** isolated by column chromatography 4-nitroimidazolyl-5-azo-(*p*-dimethylaniline) **6** was obtained.‡ Compound **6** was found to be identical (by melting point, IR and NMR spectral data) to azoimidazole obtained by the targeted synthesis from 4-nitro-5-diazoimidazole and dimethylaniline.



**Scheme 2**

In order to exclude the influence of the imidazole ring and to confirm the general character of the reaction we heated phenylazo-2-naphthol **7** with dimethylaniline for 6 h. As a result of the reaction which was carried out under the same conditions phenylazodimethylaniline **9** (30%), 2-naphthol and the starting material **7** (40%) were obtained by column chromatography

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† *General procedure for the synthesis of naphtho[2,1-e]imidazo[5,1-c]-[1,2,4]triazine* **2a**,**b**. 1-(5-Imidazoylazo)-2-naphthol **1b** (3.6 mmol) was refluxed in 15 ml of acetic acid in the presence of *p*-toluenesulfonic acid (0.29 mmol) for 12 h.

In the case of **2a**, the reaction mixture was cooled and the resulting precipitate of products **2a** and **4** was filtered off. These compounds were separated by column chromatography (ethanol–chloroform, 1:10). The eluate of **2a** was concentrated *in vacuo* to dryness. The solid residue was recrystallized from dimethylformamide to give 0.14 g (14.8%) of compound **2a**. A solution of imidazotriazine **4** was concentrated *in vacuo* to dryness and the solid residue was recrystallized from ethanol to give 0.4 g (80%) of compound **4**. The melting point and IR spectrum of this product were identical to those for the compound obtained by a known method.[6] Some physical characteristics for compound **2a**: mp 295 °C; $^1$H NMR ([$^2H_6$]DMSO) $\delta$: 8.0 (br. s, 2H, $CONH_2$), 7.62–8 .64 (m, 5H, 4–8-H), 9.37 (s, 1H, 9-H), 9.42 (d, 1H, 3-H, *J* 8.1 Hz); IR (KBr, $\nu_{max}$/cm$^{-1}$) 3400, 3100, 1660, 1520, 1490, 1310.

In the case of **2b**, the reaction mixture was cooled and the resulting precipitate was filtered off and recrystallized from dimethylformamide to give 0.85 g (90.8%) of compound **2b**. Some physical characteristics for compound **2b**: mp > 300 °C; $^1$H NMR ([$^2H_6$]DMSO) $\delta$: 7.62–8. 24 (m, 5H, 4–8 -H), 9.44 (s, 1H, 9-H), 9.24 (d, 1H, 3-H, *J* 7.9 Hz); IR (KBr, $\nu_{max}$/cm$^{-1}$) 3090, 1580, 1540, 1490, 1300.

‡ *An example of the preparation of 4-nitroimidazolyl-5-azo-(p-dimethylaniline)* **6**. 1-(4-Nitro-5-imidazoylazo)-2-naphthol (1 g, 3.6 mmol) and dimethylaniline (0.45 ml, 3.13 mmol) were refluxed in 20 ml of acetic acid in the presence of *p*-toluenesulfonic acid (0.1 g, 0.58 mmol) for 16 h. The reaction mixture was concentrated *in vacuo* to dryness. The solid residue was dissolved in ethanol–chloroform, 1:5. These compounds were separated by column chromatography. The eluate of **2b** was concentrated *in vacuo* to dryness. The solid residue was recrystallized from dimethylformamide to give 0.5 g (53.4%) of compound **2b**. The melting point, IR spectrum and NMR data of this product were identical to those for the compound obtained by the latter method. A solution of compound **6** was concentrated *in vacuo* to dryness and the solid residue was recrystallized from 50% water–ethanol and washed with diethyl ether to give 0.3 g (32.7%) of azo compound **6**. Mp 294 °C; $^1$H NMR ([$^2H_6$]DMSO) $\delta$: 3.13 (s, 2×3H, Me), 6.89 and 7.83 (d, 2×2H, AA$^1$BB$^1$, *J* 9.16 Hz), 7.79 (s, 1H, 2-H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 3420, 1570, 1540, 1380, 1310. The melting point, IR spectrum and NMR data of this product were identical to those for the compound obtained by the azo coupling of diazoimidazole **3b** with dimethylaniline in chloroform.

(Scheme 2).[§] An increase in duration of the process leads to formation of a rather complicated mixture of coloured products.

The reactions can not be carried out in the absence of *p*-toluenesulfonic acid. A plausible role for the latter involves protonation of the azo compound which initiates conversion into the diazonium salt.

Thus, we have first shown that the C-azo coupling reactions described above can be reversible under appropriate conditions.

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[§] *An example of the preparation of phenylazodimethylaniline* **9**. Phenylazo-2-naphthol **7** (1 g, 4.0 mmol) and dimethylaniline (0.54 ml, 4.23 mmol) were refluxed in 18 ml acetic acid in the presence of *p*-toluenesulfonic acid (0.1 g, 0.58 mmol) for 6 h. The reaction mixture was cooled and the resulting precipitate was filtered off and washed with benzene. The mixture of products obtained was dissolved in ethanol–water, 3:1 and separated by column chromatography. The eluate of **9** was concentrated *in vacuo* to dryness. The solid residue was triturated with a small amount of water, then filtered off and washed with diethyl ether to give 0.27 g (30%) of azo compound **9**. Mp 137 °C; $^1$H NMR ([$^2$H$_6$]DMSO) $\delta$: 3.29 (s, 2×3H, Me), 7.08 and 7.47 (d, 2×2H, AA$^1$BB$^1$, $J$ 8.04 Hz), 7.30–7.36 (m, 5H, Ph); IR (KBr, $\nu_{max}$/cm$^{-1}$ ) 1570, 1350, 1340, 1210, 1110, 790; UV ($\lambda_{max}$/nm) 584. The melting point, IR, UV and NMR data of this product were identical to those for the compound obtained by known methods.[7]

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