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Synthesis of Unsymmetrical Azabicyclo[3.3.1]nonane Structures with Different Heteroatoms

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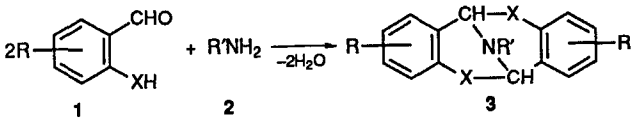
13-Substituted 11-tosyl-11,12-dihydro-6,12-imino-6*H*-dibenzo[*b,f*][1,5]thiazocines have been prepared for the first time by the reaction of 5-nitrothiosalicylaldehyde with imines of *ortho*/tosylaminobenzaldehyde.

Aromatic aldehydes **1** containing *ortho*-substituents with labile protons can react with primary amines **2** producing derivatives of azabicyclo[3.3.1]nonane **3a**, **b** (Scheme 1).



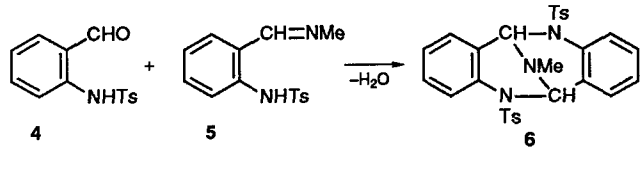
1 2 3

Scheme 1 **a**; X = S[1–3]
b; X = NTs (Ts = $SO_2C_6H_4M$-*p*)[4]
c; X = O[5]

It has been shown[4] that 13-methyl-5,6,11,12-tetrahydro-6,12-imino 5,11-ditosyl-6*H*,12*H*-dibenzo[*b,f*][1,5]diazocine **6** can also be obtained by the condensation of *o*-tosylaminobenzaldehyde **4** with *o*-tosylaminobenzylidenemethylamine **5** (Scheme 2). This reaction provides a route for the preparation of unsymmetrical derivatives of azabicyclo[3.3.1]nonane including compounds with different heteroatoms in the macrocyclic part of the molecule.

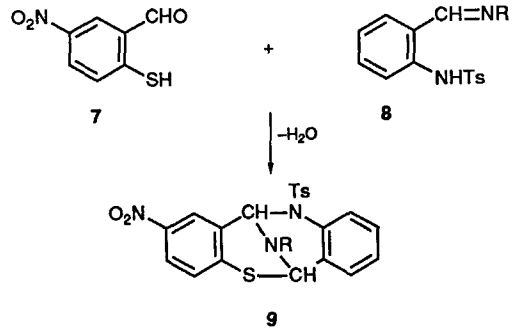
In the present paper the first examples of such reactions of 5-nitrothiosalicylaldehyde **7**† with imines **8** are reported (Scheme 3).

The reactions proceed under mild conditions. The com-



4 5 6

Scheme 2



7 8 9

Scheme 3 **a**; R = Me
b; R = Et
c; R = CH_2Ph

† Compound **7** was prepared according to ref. 2 as a solution in ether.

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pounds of type **9** were characterized by their IR (Specord IR-75, Nujol) and ^{1}H NMR spectra [Tesla-BS-567A, 100 MHz, 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as internal standard] and elemental analysis data.‡ The structure of compound **9a** was confirmed by an X-ray structural study which will be published elsewhere.

The general reaction procedure was as follows. *Ca.* 0.8 mmol of **7**[2] in 5 ml of ether was added to a solution of 0.7 mmol **8a–c**[4] in dioxane (**8a** 3 ml, **8b** 5 ml, **8c** 4 ml) and the mixture was allowed to stand for 48 h. Colourless crystals of **9a** and **9c** were collected and recrystallized from propan-2-ol–acetonitrile (1:1). In the case of **9b** the residue obtained after the evaporation of solvents from the reaction medium was subjected to column chromatography on alumina (300 × 30 mm i.d., eluent $CHCl_3$). The leading yellow fraction was collected. After the removal of solvent and recrystallization from octane colourless crystals of **9b** were obtained.

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‡ *Characterization data* for 13-methyl-2-nitro-11-tosyl-11,12-dihydro-6,12-imino-6*H*-dibenzo[*b*,*f*][1,5]thiazocine **9a**: yield 0.3 g (97%), m.p. 210–214 °C; IR ν/cm^{-1} 1605, 1572 (arom.), 1512, 1359 (NO_2), 1346, 1166 (SO_2); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3H, N—CH_3), 2.33 (s, 3H, CH_3), 5.10 (s, 1H, N—CH—N), 6.00 (s, 1H, S—CH—N), 6.95–8.40 (m, 11H, arom.).

13-Ethyl-2-nitro-11-tosyl-11,12-dihydro-6,12-imino-6*H*-dibenzo-[*b*,*f*][1,5]thiazocine **9b**: yield 0.1 g (32%), m.p. 203–205 °C; IR ν/cm^{-1} 1605, 1572 (arom.), 1512, 1359 (NO_2), 1346, 1166 (SO_2); ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.43 (q, 2H, CH_2), 5.19 (s, 1H, N—CH—N), 5.85 (s, S—CH—N), 6.85–8.31 (m, 11H, arom.).

13-Benzyl-2-nitro-11-tosyl-11,12-dihydro-6,12-imino-6*H*-dibenzo-[*b*,*f*][1,5]thiazocine **9c**: yield 0.3 g (92%), m.p. 232–234 °C; IR ν/cm^{-1} 1625, 1605, 1599, 1572 (arom.), 1512, 1359 (NO_2), 1346, 1166 (SO_2); ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H, CH_3), 3.68 (s, 2H, CH_2), 5.08 (s, 1H, N—CH—N), 6.26 (s, 1H, S—CH—N), 6.70–8.48 (m, 11H, arom.).

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