

SHORT
COMMUNICATIONS

Ionic Hydrohetarylation of *N*-Benzylideneanilines in the System Sodium Tetrahydridoborate–1,3-Benzodithiolium Salt

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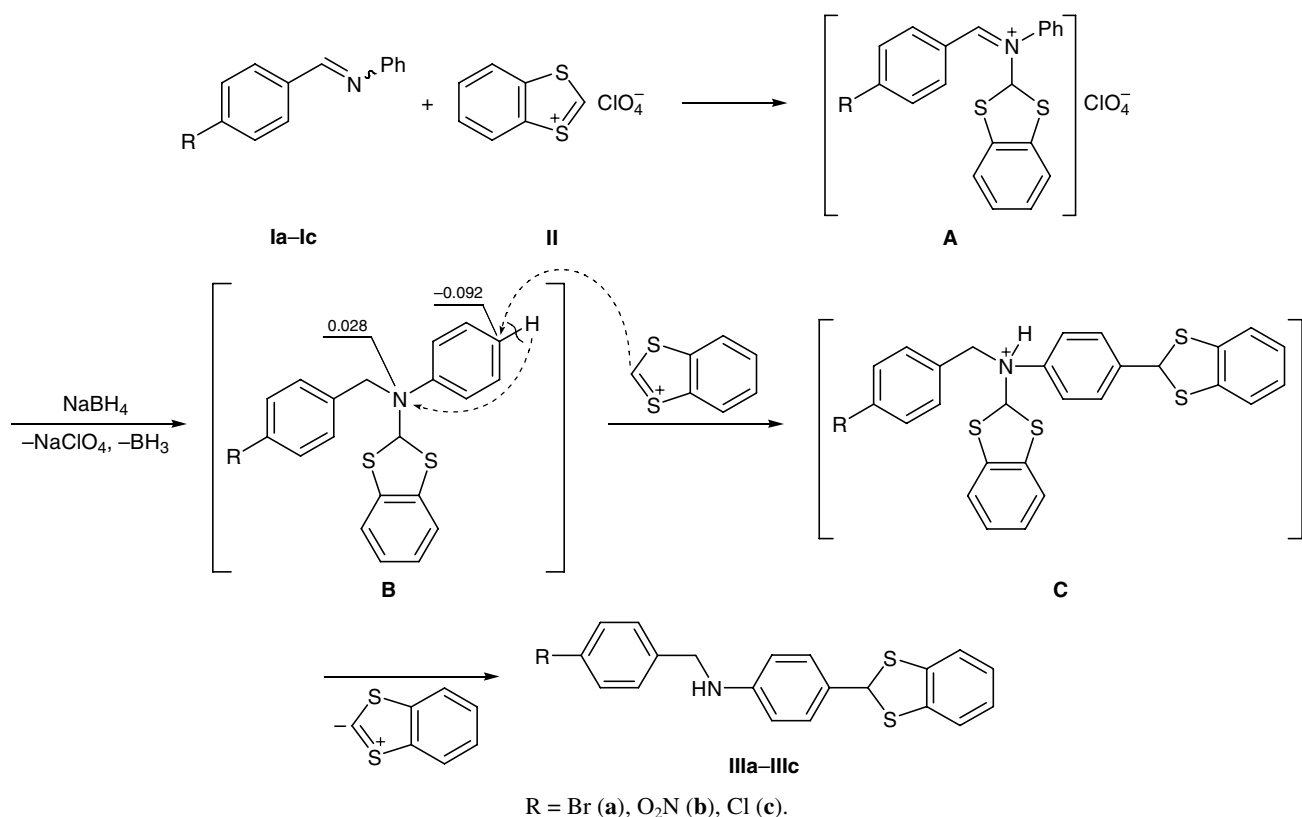
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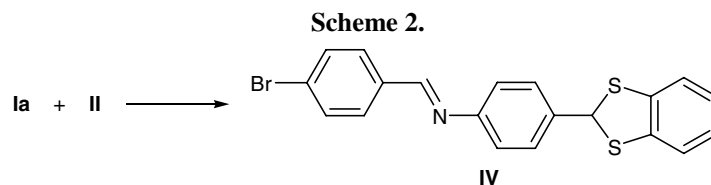
Heterocyclic H-nucleophiles simulating the behavior of NADH, specifically *N*-methyl-9,10-dihydroacridine and its heteroanalogs (xanthene, 1,3-benzodithiol), are capable of reducing triphenylmethyl cation to triphenylmethane [1, 2]. It might be presumed that 1,3-benzodithiole would behave in a way similar to xanthene in reactions with such hydride ion acceptors as protonated imines. It is known that reductive xanthenylation [3] is accompanied by formation of secondary aromatic amines having a xanthene fragment. We

have found that analogous compounds possessing a 1,3-benzodithiol fragment can be obtained by ionic hydrohetarylation of Schiff bases **Ia–Ic** in the system NaBH₄–1,3-benzodithiolium perchlorate (**II**) but not via direct reaction of Schiff base with 1,3-benzodithiole; these findings indicate that 1,3-benzodithiole is a weaker donor of hydride ion.

As shown in [2], *N*-substituted anilines react with 1,3-benzodithiolium tetrafluoroborate to give stable tertiary amines. However, as a result of ionic hydrohet-

Scheme 1.





arylation we obtained secondary aromatic amines, *N*-benzyl-4-(1,3-benzodithiol-2-yl)anilines **IIIa–IIIc** (Scheme 1). In the ^1H NMR spectra of **IIIa–IIIc**, the signal from the CH proton in the heteroring is displaced upfield by 1 ppm, and the CH_2 signal appears as a singlet (no coupling with the NH proton is observed; cf. [4]).

Presumably, the reaction of Schiff bases **Ia–Ic** with 1,3-benzodithiolium ion begins with formation of iminium salt which is reduced with NaBH_4 to give tertiary amine **B**; electrophilic attack on the latter by the second 1,3-benzodithiolium ion at the *para* position of the benzene ring in the aniline fragment leads to quaternary ammonium ion **C** which is then converted into the final product via elimination of 1,3-benzodithiolium ion. This reaction scheme is well consistent with the data reported in [2] for the reaction of *N,N*-dimethylaniline with 1,3-benzodithiolium salt **II** and the results of AM1 quantum-chemical calculations.

Treatment of 1,3-benzodithiolium salts with a strong base, triethylamine ($\text{p}K_a$ 10.87), is known to promote its dimerization with formation of dibenzotetraphthalfulvalene [2]. We have found that the reaction of Schiff base **Ia** ($\text{p}K_a$ 9.31) [5] with an equimolar amount of salt **II** in boiling THF in the absence of NaBH_4 (reaction time 1 h) yields *N*-(4-bromophenylmethylidene)-4-(1,3-benzodithiol-2-yl)aniline (**IV**) (Scheme 2).

4-(1,3-Benzodithiol-2-yl)-*N*-(4-bromobenzyl)aniline (IIIa). Sodium tetrahydridoborate, 0.15 g (4 mmol), was added in three portions over a period of 1.5 h to a mixture of 0.52 g (2 mmol) of Schiff base **Ib** and 0.51 g (2 mmol) of perchlorate **II** in 30 ml of THF under stirring at room temperature. The mixture was then pured into water, and the precipitate was filtered off and recrystallized from ethanol. Yield 0.39 g (47%), light pink crystals, mp 149–151°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.13 s (1H, NH), 4.21 s (2H, CH_2), 6.15 s (1H, 2-H), 6.94–7.39 m (12H, H_{arom}). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 414 (4.0). Found, %: C 57.01; H 3.90; N 3.08; S 16.00. $\text{C}_{20}\text{H}_{16}\text{BrNS}_2$. Calculated, %: C 57.97; H 3.90; N 3.39; S 15.47. M 414.38.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

4-(1,3-Benzodithiol-2-yl)-*N*-(4-nitrobenzyl)aniline (IIIb). Yield 16%, light yellow crystals, mp 215–217°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.30 s (1H, NH), 4.40 s (2H, CH_2), 6.13 s (1H, 2-H), 6.94–7.46 m (12H, H_{arom}). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 380 (9.0), 258 (1.0), 244 (2.0), 229 (5.0), 227 (10.2), 153 (100.0), 151 (5.1), 136 (2.1), 122 (6.2).

4-(1,3-Benzodithiol-2-yl)-*N*-(4-chlorobenzyl)aniline (IIIc). Yield 52%, light pink crystals, mp 148–149°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.15 s (1H, NH), 4.23 s (2H, CH_2), 6.15 s (1H, 2-H), 6.94–7.31 m (12H, H_{arom}). Mass spectrum, m/z (I_{rel} , %): $[M]^+$ 370 (37.9), 258 (1.7), 244 (8.3), 229 (6.0), 216 (14.7), 153 (100.0), 140 (2.4), 125 (86.5), 11 (1.5).

4-(1,3-Benzodithiol-2-yl)-*N*-(4-bromobenzylidene)aniline (IV). Yield 92%, light brown crystals, mp 157–158°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 6.16 s (1H, 2-H), 6.98–7.70 m (12H, H_{arom}), 8.30 s (1H, $\text{CH}=\text{N}$). Found, %: C 58.27; H 3.34; N 2.29; S 16.91. $\text{C}_{20}\text{H}_{14}\text{BrNS}_2$. Calculated, %: C 58.25; H 3.43; N 3.40; S 15.60.

The ^1H NMR spectra were recorded on a Varian Mercury-300 spectrometer at 300 MHz. The mass spectra were obtained on an HP 6890–MSD 5973 instrument.

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