On the Electrochemical Reduction of Benzo-1,2,3-triazin-4(3*H*)-ones

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Some years ago a reduction route (Scheme 1) of benzo-1,2,3-triazin-4(3*H*)-one (*1a*) to indazolinone (*2a*) was proposed in a review;[1] in a recent paper [2] Scheme 1 was rejected and another route proposed (Scheme 2) in which the ring closure occurred between N^1 and N^3.

According to Scheme 1, N^3 is lost, whereas N^3 is eliminated in Scheme 2. An obvious way to test the correctness of the schemes would be to reduce a benzo-1,2,3-triazin-4(3*H*)-one substituted at N^3. According to Scheme 1, the products would be *2a* and an amine, whereas Scheme 2 predicts a 2-substituted indazolinone and ammonia as products.

This communication reports on the electrochemical reduction of 3-phenylbenzo-1,2,3-triazin-4(3*H*)-one (*1b*) and related compounds in acid solution and in DMF.

Results and discussion. Electrochemical reduction of *1b* in 0.5 M aqueous-alcoholic hydrochloric acid at a mercury electrode yielded *2a* (80 %) and aniline (*6*) (80 %) together with benzanilide (*7*) (18 %); the reaction mixture was analyzed by HPLC, and besides the major products traces of two unidentified products were detected, but none could be ascribed to 2-phenylindazolinone-3. The composition of the reaction mixture was not dependent on the temperature (between 5 and 55 °C) to any appreciable degree, but the pH had some influence (Table 1); at low pH the yield of (*7*) increased.

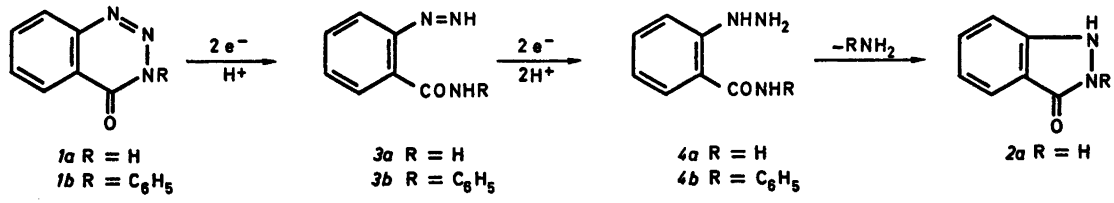
In an aprotic solvent, *N*,*N*-dimethylformamide (DMF), the only isolated product (90 % yield) from the reduction of *1b* was *7*; *7* was also obtained from the reduction of 2'-methoxycarbonyldiazoaminobenzene (*8*) in DMF; a base-catalyzed ring closure of *8* to *1b* may occur before or during the reduction.

Table 1. Yields of indazolinone (*2a*), aniline (*6*) and benzanilide (*7*) from the electrolytic reduction of 3-phenylbenzo-1,2,3-triazin-4(3*H*)-one (*1b*) in 60 % ethanol at 19 °C.

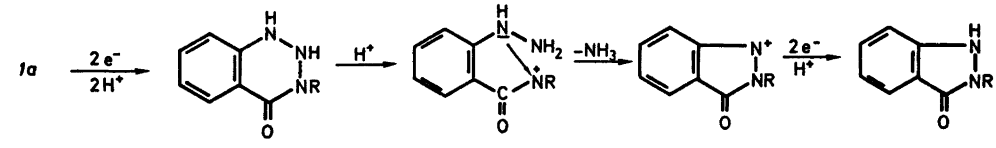
Medium	Yield of *2a*/%	Yield of *6*/%	Yield of *7*/%
Acetate buffer pH 4.8	83	85	11
0.1 M HCl	83	83	11
0.5 M HCl	80	80	18
2 M HCl	51	51	46
4 M HCl	24	24	74

The isolation of *2a* and *6* from the reduction of *1b* in acid solution is compatible with Scheme 1, but not with Scheme 2. The formation of *7* in good yield cannot be explained by any of the intermediates proposed in Scheme 2, whereas a loss of molecular nitrogen from *3b* would form *7*.

The results obtained for the reduction of *1b* thus suggest that for *1b* Scheme 1, which is analogous to a large number of other electrochemically induced ring closure reactions,[1] is essentially correct and that *3b* and *4b* are intermediates; it seems probable that it also describes the reduction of other benzo-1,2,3-triazin-4(3*H*)-ones reasonably well. Scheme 1 is not, however, a detailed description of the reaction; such a description would include *5b* as an intermediate between *1b* and *3b* as well as several steps in the ring closure and elimination reactions. The ring closure probably takes place



Scheme 1.



Scheme 2.

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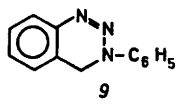
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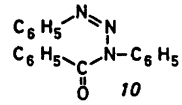
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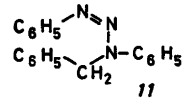
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by attack of N^3 on the carbonyl group followed by acid–catalyzed elimination of RNH_2.

It seems plausible that an acid–catalyzed ring opening of *5a* to *3a* takes place and that besides a direct reduction of *3a* at the electrode an electron transfer in solution occurs, so the following reaction [2] takes place

5a + *3a* ⇌ *1a* + *4a*

The regenerated *1a* is then reduced at the electrode. The relative importance of the direct and indirect reduction of *3a* might be pH-dependent. The polarographic results [2] are in agreement with such an interpretation.

3-Phenylbenzo-1,2,3-triazine (*9*) was reduced in acid aqueous-alcoholic solution and the products analyzed by HPLC; *N*-benzylaniline (*12*) (15 %) was isolated and at least eight other compounds, with no apparent main product, were detected, but not identified. Attempts to benzoylate the reaction mixture in order to isolate *N*-benzoyl-2-phenylindazoline [2] were not successful.

Reduction in acetate buffer of 1,3-diphenyl-1-benzoyltriazene (*10*) yielded benzanilide and phenylhydrazine, whereas 1-benzyl-1,3-diphenyltriazene (*11*) gave aniline, benzylaniline, and 1,1-benzylphenylhydrazine. The results from the open-chain triazenes thus agree well with those from the analogous heterocyclic compounds.

Experimental. Materials. The following compounds were prepared according to the references given: 3-Phenylbenzo-1,2,3-triazin-4(3*H*)-one (1b),[3] 3-phenylbenzo-1,2,3-triazine (*9*),[2] 1-benzyl-1,3-diphenyltriazene (*11*),[4] 1-benzoyl-1,3-diphenyltriazene (*10*).[5]

Reduction of 1b *(1). 1b* (0.2 g) was reduced in aqueous 0.5 M hydrogen chloride containing 50 % ethanol at −0.6 V (*vs.* saturated calomel electrode), $n = 3$. After the reduction the catholyte was evaporated *in vacuo*, the residue dissolved in methanol and analyzed by HPLC on a 30 cm RP-18 column with 40 % aqueous methanol as eluent, pressure 170 atm. Retention time: Indazolinone (*2a*), 4.7 min, aniline hydrochloride (*6*), 5.8 min, benzanilide (*7*), 8.8 min. Yields, see Table 1. The concentration of aniline was also determined spectrophotometrically after diazotization and coupling with naphthylethylenediamine.

Reduction of 1b *(2). 1b* (0.5 g) was reduced at −1.2 V in DMF/0.1 M tetrabutylammonium iodide, $n = 0.95$. After reduction the catholyte was diluted with water and extracted with diethyl ether, which was washed with water, dried and evaporated leaving 0.43 g of benzanilide.

Reduction of 9. *9* (0.2 g) was reduced in 1 M HCl containing 50 % ethanol at −0.7 V, $n = 2.7$. The catholyte was concentrated to one third of the volume, made alkaline, and extracted with ether. In the ether layer *N*-benzylaniline (*12*) (15 %) was identified by NMR spectroscopy and TLC; the presence of at least eight other products was shown by TLC. On separation on a column of silica with dichloromethane *N*-benzylaniline was isolated; unidentified products with *m/e* 253 and 303 were also isolated. Attempts were made to benzoylate the crude product mixture, obtained by evaporation of the catholyte, but neither this nor acetylation were successful. Neither 2-phenylindazoline nor its *N*-benzoyl derivative [2] were isolated.

Reduction of 10. *10* (0.50 g) was reduced in an acetate buffer containing 50 % ethanol and 20 % *N*,*N*-dimethylformamide at −1.50 V, $n = 2.0$. After reduction the catholyte was cooled to −15 °C and on standing *7* crystallized; *7* was collected and recrystallized from ethanol, 250 mg. The filtrate was made alkaline and extracted with diethyl ether; evaporation of the solvent left phenylhydrazine.

Reduction of 11. *11* (0.5 g) was reduced in an acetate buffer containing 50 % ethanol and 20 % DMF at 1.30 V, $n = 3$. The ethanol was removed by distillation, water and some acetone added, the solution made alkaline and extracted with diethyl ether. The residue from the ether extract was separated on a column of silica; isolated were benzylaniline, aniline and acetone 1-benzyl-1-phenylhydrazone; the latter was identified by comparison of the NMR and IR spectra with those of authentic acetone 1-benzyl-1-phenylhydrazone.

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