

Electrochemical Reduction of Some Benzotriazoles in Protic and Aprotic Media

Steen Utrup Pedersen and Henning Lund

Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

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1-Phenylbenzo-1,2,3-triazole is reduced polarographically in aqueous acidic solution in a diffusion-controlled four-electron reaction to *o*-hydrazinodiphenylamine; in aprotic medium the reduction requires approximately 1 F mol^{-1} , and a mixture of carbazole and diphenylamine is obtained. 1-Substituted benzotriazoles are generally reduced in *N,N*-dimethylformamide (DMF) in the presence of phenol to substituted anilines, whereas 2-substituted benzotriazoles are reduced in DMF to a relatively stable anion radical. In the presence of phenol the dihydro derivative is obtained; under work-up it is oxidized to the benzotriazole. In the presence of acetic anhydride, benzotriazole is reduced to 1,2,3-triacetyldihydrobenzotriazole.

Benzotriazole (**1a**) and related compounds have previously been investigated by polarography¹⁻³ and by preparative reduction.² It was found that **1a** was reduced in hydrochloric acid in a four-electron reaction to *o*-aminophenylhydrazine (**4a**).² This was later confirmed, and **4a** was employed for the synthesis of benzo-1,2,4-triazines.⁴

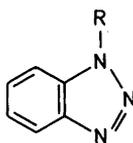
It has been argued³ that the reduction of **1a** at the dropping mercury electrode was not the result of a direct electron transfer to **1a**, but proceeded by an indirect reduction by electrogenerated hydrogen. Catalytic reduction of an organic substrate at a mercury electrode seems rather unlikely, but to clarify the matter 1-phenylbenzotriazole (**1c**) was investigated polarographi-

cally. **1c** was chosen as it is reduced at less negative potentials than **1a**.

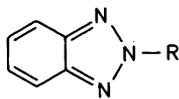
Benzotriazoles have not been studied electrochemically in aprotic media, so the compounds shown below were investigated by cyclic voltammetry (CV), derivative cyclic voltammetry (DCV) and preparative reduction with and without addition of proton donors or electrophiles.

Results

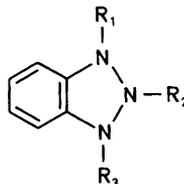
CV of benzotriazole (**1a**) in DMF showed a reduction peak at $-1.83 \text{ V vs. Ag/AgI}$; the reverse trace showed a "reduction" peak, the nature of which was not investigated further. **1a** in DMF is



- 1a:** R = H
1b: R = CH₃
1c: R = C₆H₅
1d: R = COCH₃



- 2a:** R = CH₃
2b: R = C₆H₅



- 3a:** R¹ = R³ = H, R² = CH₃
3b: R¹ = R³ = H, R² = C₆H₅
3c: R¹ = R² = R³ = COCH₃

a stronger acid than phenol [$\text{p}K_{\text{a}}(\mathbf{1a}) = 12.6$,⁵ $\text{p}K_{\text{a}}(\text{phenol}) = 18.03$,⁶ (DMSO)] so protonation of $\mathbf{1a}^-$ by $\mathbf{1a}$ is probably occurring. On preparative reduction, a substantial yield of $\mathbf{1a}$ was found at work-up; the anion of $\mathbf{1a}$ was not reducible at the applied potential. In the presence of an excess of phenol the peak height in CV increased corresponding to $n = 2$, and on preparative reduction under such conditions aniline (yield > 70%) was the main product.

Reduction of $\mathbf{1a}$ in the presence of an excess of acetic anhydride yielded 1,2,3-triacetyldihydrobenzotriazole ($\mathbf{3a}$). This, together with 1,3-dihydro-1,3-dihydroxy-2-phenylbenzotriazole,⁷ seem to be the only stable derivatives of dihydrobenzotriazole isolated so far.

$\mathbf{1c}$ was reduced polarographically in aqueous acidic solution giving a wave which had a tendency to exhibit a maximum; the height of the wave increased linearly with the height of the mercury reservoir, indicating a diffusion-controlled process. Preparative reduction in 6 N hydrochloric acid consumed 4.2 F mol^{-1} ; the product, presumably 2-(phenylamino)phenylhydrazine, formed coloured substances during reduction and on work-up, probably due to the lower basicity of the compound compared to 2-aminophenylhydrazine. This might result in a loss of hydrogen chloride on evaporation of the solvent in vacuum, giving the more easily oxidizable diphenylamine derivative.

$\mathbf{1b}$ exhibited under aprotic conditions a reversible voltammogram with a standard potential of $-2.16 \text{ V vs. Ag/AgI}$. $\mathbf{1c}$ exhibited totally irreversible CV behaviour under similar conditions at a scan-rate of 0.4 V s^{-1} . The $v_{1/2}$ for $[\mathbf{1c}] = 1.0 \text{ mM}$ was found to be 25 Vs^{-1} in DCV ($k_{\text{EC}} = 76 \text{ s}^{-1}$).⁸ This $v_{1/2}$ increased to 300 V s^{-1} when 5 mM phenol was added ($k_{\text{EC}} = 912 \text{ s}^{-1}$). In the presence of a two-fold excess of phenol, $\mathbf{1b}$ was reduced irreversibly. Electrolysis of $\mathbf{1b}$ with a two-fold excess of $\mathbf{2}$ in phenol produced *N*-methylaniline. The current consumption was 2.4 F mol^{-1} .

The isolated products from the electrolysis of $\mathbf{1c}$ under aprotic conditions were approximately equal amounts of carbazole ($\mathbf{5}$) and diphenylamine ($\mathbf{6}$). The consumed current correspond to 1.2 F mol^{-1} . The same reduction under protic conditions with excess of phenol showed $n = 2.4$, and only diphenylamine was isolated. The reduction of $\mathbf{1c}$ by sodium in liquid ammonia resulted in formation of only diphenylamine.

The reduction of $\mathbf{1c}$ to $\mathbf{6}$ requires $n = 2$, whereas the formation of $\mathbf{5}$ is not a reduction ($n = 0$); carbazoles may be synthesized by the Graebe-Ullmann pyrolysis of suitable 1-arylbenzotriazoles.⁹ The formation of carbazole is akin to the reductive cyclization of e.g. 5-(2-chlorophenyl)-1-phenylpyrazole to pyrazolo[1,5-*f*]phenanthridine.¹⁰

1-Acetylbenzotriazole ($\mathbf{1d}$) was reduced in a one-electron irreversible reaction. The peak potential was $-1.28 \text{ V vs. Ag/AgI}$ at a scan-rate of 0.4 V s^{-1} . Addition of an excess of acetic anhydride caused the peak current to increase to a value corresponding to $n = 2$. The peak potential shifted 50 mV to a more negative value. A preparative electrolysis under aprotic conditions resulted in the formation of *N*-acetylaniline.

Electrolysis of $\mathbf{1d}$ with excess of acetic anhydride consumed 1.8 F mol^{-1} and the main product was *N*-acetylaniline; some 1,2,3-triacetyl-dihydrobenzotriazole was also found.

2-Methylbenzotriazole ($\mathbf{2a}$) and 2-phenylbenzotriazole ($\mathbf{2b}$) exhibited reversible voltammograms in CV in DMF. $E_{\text{p,red}}$ of $\mathbf{2a}$ was $-1.88 \text{ V vs. Ag/AgI}$, whereas $\mathbf{2b}$ showed two reversible peaks at $E_{\text{p,red}}(1) = -1.65 \text{ V}$ and $E_{\text{p,red}}(2) = -2.27 \text{ V}$. On addition of an excess of phenol, irreversible voltammograms were obtained and the peak height of the first peak corresponded to $n = 2$. Preparative reduction in the presence of phenol as proton donor (n between 1 and 2) gave a product which on work-up yielded the starting material. Presumably the 2-substituted dihydrobenzotriazoles ($\mathbf{3a}$ and $\mathbf{3b}$) were formed on reduction of both $\mathbf{2a}$ and $\mathbf{2b}$, but $\mathbf{3a}$ and $\mathbf{3b}$ are easily reoxidized during work-up. In aqueous solution $\mathbf{2a}$ has been reduced to $\mathbf{3a}$, which could be re-oxidized to $\mathbf{2a}$;² addition of hydrochloric acid to a solution of $\mathbf{3a}$ resulted in formation of 1-(2-aminophenyl)-2-methylidimide.²

Discussion

The polarographic and preparative results for the reduction of $\mathbf{1c}$ give no indication that this should be reduced by electrogenerated hydrogen³ rather than by electron transfer to the protonated $\mathbf{1c}$, and it seems very unlikely that $\mathbf{1a}$ under similar conditions should be reduced by a route completely different from that for $\mathbf{1c}$.

The anion radicals of 2-substituted benzotriazoles are quite stable in aprotic solutions. If

strong proton donors are present, the 2-substituted dihydrobenzotriazoles can be formed; however, these are readily oxidized to the starting material during work-up.

1c is reduced to equal amounts of carbazole ($n = 0$) and diphenylamine ($n = 2$) in a one-electron reduction under aprotic conditions. It seems likely that this particular product distribution is not a consequence of two competing reaction paths, but rather the outcome of a multi-step reaction sequence. The product-determining step could be a disproportionation, a hydrogen abstraction or a proton transfer reaction. A preliminary mechanism is shown in Scheme 1.

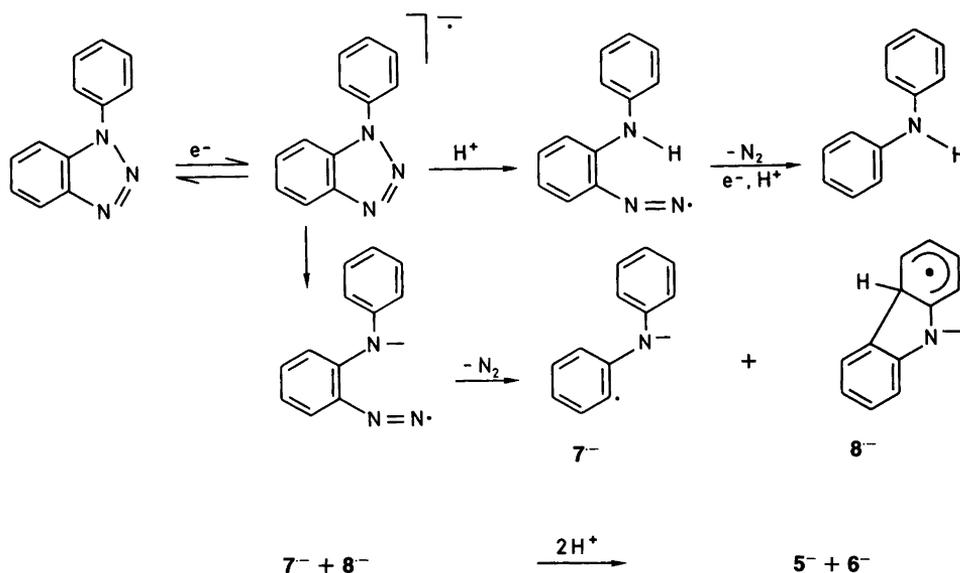
When a proton donor is present in excess, only diphenylamine is formed; the product-determining step may therefore be a proton transfer reaction. The addition of phenol (1:5) increased the k_{EC} by a factor of 12, and for **1b** the reduction changed from a reversible one-electron reduction to an irreversible two-electron reduction when phenol was added. It seems likely that the rate-determining step is the opening of the triazole ring. The later loss of N_2 , which is similar to the cleavage reaction in the reduction of arenediazonium salts, is probably very fast.

The anion radical 7^- may cyclize to 8^- or add a hydrogen atom to give 6^- . As the product ratio (5:6) consistently is 1:1, it seems not unlikely that

the disproportionation is a hydrogen atom transfer from 8^- to 7^- , thus forming 5^- and 6^- . This proposal is in accordance with the known facts, but should be regarded as a working hypothesis.

A proton donor can protonate the anion radical of the benzotriazole, and the resulting benzotriazole radical is likely to ring-open faster than the anion radical because the latter compound ring-opens to the high-energy aniline anion. This model explains why there are such large differences in rate under aprotic and protic conditions.

The difference in rate for the different 1-substituted benzotriazole under aprotic conditions can also be understood from this model. When the anion radical of the benzotriazole undergoes the ring-opening, a substituted aniline anion is formed. A measure of the stability of the aniline anion in DMF is the pK_a value for the corresponding substituted aniline. Diphenylamine [$pK_a = 25$, (DMSO)¹¹] is a much stronger acid than *N*-methylaniline and aniline [$pK_a = 30.7$, (DMSO)¹²] and a similar difference must be expected in DMF; consequently the ring-opening and aniline-anion formation for diphenylamine occurs more readily than for *N*-methylaniline. Aniline and *N*-methylaniline have similar pK_a values, but benzotriazole can act as proton donor in a self-protonation reaction, the reaction of **1a** thus being more complicated than that of **1b**.



Scheme 1.

Experimental

Reagents. All the substituted benzotriazoles except 1-phenylbenzotriazole were synthesized according to the procedures given in Ref. 2 and references therein. 1-Phenylbenzotriazole was synthesized by the method of Reynolds.¹³ *N,N,N'*-Triacetyldihydrobenzotriazole was obtained by reduction of 2 g (0.22 M) of **1a** and 15 ml of acetic anhydride (2.12 M) in 80 ml of DMF/TBAI (0.1 M) at a mercury pool cathode at -1.3 V vs. Ag/AgI ($n = 2.06$). The DMF was evaporated and the product extracted with diethyl ether; the ether phase was washed with water, dried and evaporated. The product was recrystallized from CH_2Cl_2 . *N,N',N''*-Triacetyldihydrobenzotriazole (m.p. 117.2 – 117.5°C) was identified by NMR, MS and IR. ^1H NMR (300 MHz, CDCl_3): δ 2.320 (3H, s), 2.392 (6H, s), 7.2–7.7 (4H, m). MS, IP 70 eV; m/e (% rel. int.): 204 (16), 162 (44), 120 (100), 92 (18), 66 (20), 44 (45). IR (KBr) cm^{-1} : 3400 (m), 1750 (s), 1600 (m), 1480 (s), 1360 (s), 1240 (s), 1020 (s), 960 (m), 840 (w), 750 (s).

Dr. R. G. Hazell has determined the X-ray structure of **3c**;¹⁴ the structure is shown in Fig. 1.

Cells and electrodes. The preparative reductions were performed in an H-cell with a cathodic compartment of either 150 ml or 75 ml. The cathode was a mercury pool, the anode a carbon stick, and the reference electrode a silver wire (Ag/AgI). Cyclic voltammetry was performed using a 50 ml beaker with 25 ml of DMF solution. The cathode was a hanging mercury drop electrode,

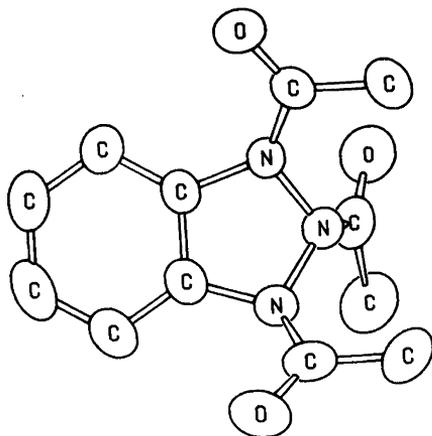


Fig. 1. ORTEP drawing of compound **3c**.

the anode a platinum wire and the reference electrode a silver wire in DMF/TBAI, 0.1 M I^- .

Instrumentation. The potentiostat used in the preparative electrolysis was from Juul-Electronic, Copenhagen. The potentiostat/ramp-generator used for cyclic voltammetry was of our own construction. The cyclic voltammograms were recorded on a HP 7045A X-Y recorder. DCV were performed in Dr. O. Hammerich's laboratory with the equipment described in Ref. 15.

NMR. Spectra were either recorded on a 300 MHz Varian XL-300 spectrometer or for routine analysis on a Varian CFT 20 NMR spectrometer.

Gas chromatography. The gas chromatograph was an HP 5496 and the column either an SP 2340 with the following temperature program: 140°C (2 min) \rightarrow 220°C with 5°min^{-1} , or a PEG 20 M cap. col. with the following temperature program: 120°C (2 min) \rightarrow 220°C with 7°min^{-1} .

Mass spectroscopy. The mass spectra were obtained on a VG 7070F spectrometer equipped with an acquisition system of our own construction including an Olivetti M24 PC.

IR. Spectra were recorded on a Nicolet 5-MX-S instrument.

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