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Electroörganic Preparations. XXXVII. Electrosynthesis of Cinnolines by Reductive Ring Closure of Dinitrocompounds

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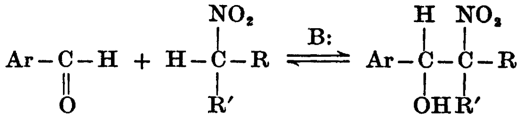
Cinnoline and its 3-methyl and 3-phenyl derivatives have been prepared in good yields by controlled potential reduction of suitable dinitroalcohols; the reduction yields the corresponding dihydroxylaminoalcohols which in presence of oxygen condense in a base catalysed reaction to the cyclic compounds. The 1-*N*-oxide was also formed in appreciable amounts in the preparation of 3-phenylcinnoline besides some 2,1-benzisoxazole (anthranil). The yields of cinnolines were found to depend mainly on the pH and the temperature during the electrolysis.

Among the benzodiazines the cinnolines are some of the least accessible.[1] Most synthetic routes involve several steps which besides being tedious often result in low over-all yields. For example, the preparation of 3-phenylcinnoline *via* *N*-benzylideneamino isatin involves five consecutive steps starting with benzaldehyde phenylhydrazone.[2] Controlled potential electrolysis is a valuable tool to induce ring closure reactions[3,4] by bringing the reaction centres in suitable oxidation states, and below is reported an application of this method for a convenient synthesis of 3-substituted cinnolines.

RESULTS AND DISCUSSION

Dinitroalcohols. As starting materials serve the dinitroalcohols I (R = H) which are easily available by the Henry addition between *o*-nitrobenzaldehyde and primary or secondary nitroalkanes.



$$\mathrm{Ar-\underset{\underset{O}{\|}}{C}-H} + \mathrm{H-\overset{\overset{NO_2}{|}}{\underset{\underset{R'}{|}}{C}}-R} \xrightleftharpoons{\mathrm{B:}} \mathrm{Ar-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{NO_2}{|}}{\underset{\underset{R'}{|}}{C}}-R}$$

Ar = 2-nitrophenyl

I

Ia, R = R′ = H
Ib, R = H, R′ = Me
Ic, R = R′ = Me
Id, R = H, R′ = Ph

The presence of the *o*-nitro group made the dinitroalcohols (I) stable in solution and they showed no tendency to eliminate water with the formation of β-nitrostyrenes contrarily to the corresponding unsubstituted nitroalcohols derived from benzaldehyde.[5,6] Compounds Ib and Id were obtained as 1:1 and 1:2 mixtures of the (±)-*erythro* and (±)-*threo* stereoisomers, respectively, by using triethylamine as the basic catalyst for the addition. The stereoisomeric dinitroalcohols were separated by column chromatography on silica. Acetic acid was added to the stationary phase and to the developing solvent; otherwise, the dinitroalcohols were partly reconverted to *o*-nitrobenzaldehyde and the parent nitroalkane.

The NMR spectra of the investigated dinitroalcohols in deuteriochloroform solution are collected in Table 1. The stereochemical assignments of the *erythro*- and *threo*-isomers rest upon a comparison between the data in Table 1 and the NMR spectrum (see Experimental) of (±)-*threo*-α-(1-nitrobenzyl)benzyl alcohol, the stereochemistry of which is well established.[7,8] Although there are considerable differences in the δ-values of the H^a protons in the stereoisomeric dinitroalcohols (due to the *o*-nitro

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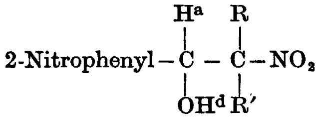
Table 1. NMR parameters of *o*-nitro-α-(1-nitroalkyl/aralkyl)benzyl alcohols, I. ($CDCl_3$; chemical shift values in δ (ppm); coupling constants J in Hz; TMS as internal standard).



$$\text{2-Nitrophenyl}-\underset{OH^d}{\overset{H^a}{C}}-\underset{R'}{\overset{R}{C}}-NO_2$$

Compound	R	R′	H^a	H^b	H^c	H^d	Arom. protons	J_{ab}	J_{ac}	J_{ad}	J_{bc}
Ia	H^b	H^c	5.99	4.83	4.56	3.49	7.3−8.1	2.4	9.2	–	−13.7
erythro-Ib	H^b	$CH_3{}^c$	6.08	4.97	1.51	3.32	7.3−8.2	3.0	–	4.5	7
threo-Ib	H^b	$CH_3{}^c$	5.68	4.97	1.44	3.55	7.3−8.2	7.0	–	5.5	7
Ic	$CH_3{}^b$	$CH_3{}^c$	6.28	1.38	1.52	3.39	7.3−8.0	–	–	–	–
erythro-Id	H^b	C_6H_5	6.32	5.93		3.45	7.1−8.2	4.2	–	–	–
threo-Id	H^b	C_6H_5	6.38	5.87		4.08	7.1−8.2	9.5	–	–	–

group) and the reference compound, it seems characteristic that the compound which was assigned the *threo*-Id structure had a coupling constant J_{ab}, identical with the value (9.5 Hz) found for the (±)-*threo*-α-(1-nitrobenzyl)benzyl alcohol. The coupling constants between H^a and H^b in benzene-d_6 of both *threo*-Id and the reference compound were practically unaltered from the values found in deuteriochloroform. In dimethyl sulfoxide-d_6, the H^a and H^b protons of *threo*-Id by chance had the same δ-value which excluded the determination of the coupling constant. For both the *erythro*-Id and the reference compound, however, only a small variation in the value of J_{ab} was observed in this solvent.

The assignment of the *erythro*- and *threo*-isomers of Ib was more uncertain, but was based on a comparison of the coupling constants and also on the chromatographic behaviour of *erythro*- and *threo*-Id. The J_{ab} coupling constants seem to indicate preference for all the stereoisomeric dinitroalcohols of conformations which enable a hydrogen bonding between the hydrogen of the alcohol function and the aliphatically bound nitro group.

Polarographic investigation. The dinitroalcohols show two well-defined polarographic waves at pH < 7; in Fig. 1 are depicted the half-wave potentials of (±)-*erythro*-*o*-nitro-α-(1-nitroethyl)-benzyl alcohol (*erythro*-Ib) in dependence of pH in acidic to neutral solution. At higher pH a third pH-independent wave with $E_{\frac{1}{2}} = -0.56$ V (*vs.* SCE) grows up which probably is due to the reduction of the *o*-nitro group of *o*-nitrobenzaldehyde generated by a reversal of the Henry addition. Both waves were shown by controlled potential electrolysis to be four-electron waves. The half-wave potential of the first wave which has a slope of the $E_{\frac{1}{2}}$-pH curve of 0.086 V/pH corresponds to a reduction of the "aromatic" *o*-nitro group to a hydroxylamino function,[9] while the second wave corresponds to a reduction of the "aliphatic" nitro group to the hydroxylamino stage (Scheme 1).

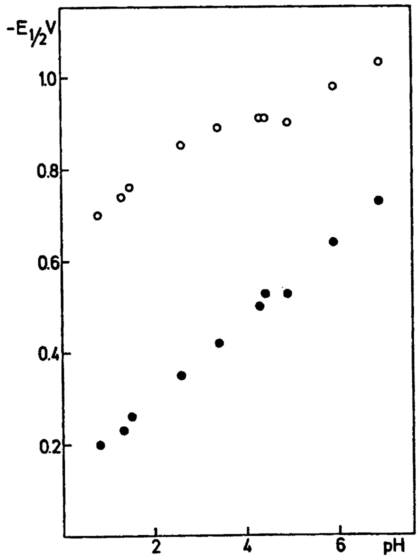
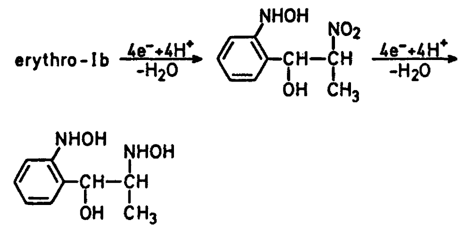


Fig. 1. Half-wave potentials (V *vs.* SCE) of (±)-*erythro*-*o*-nitro-α-(1-nitroethyl)benzyl alcohol in 40 % aqueous ethanol. Concentration 80 mg/l. ● ○, Data of first and second wave, respectively.



Scheme 1.

Although the dihydroxylamino compound thus produced apparently was quite stable in solution when kept under nitrogen, no attempt was made to isolate this strongly hydrophilic product neither in analytical nor in preparative scale.

Table 2 shows the half-wave potentials of the investigated dinitroalcohols I in an acetate buffer at pH 5.

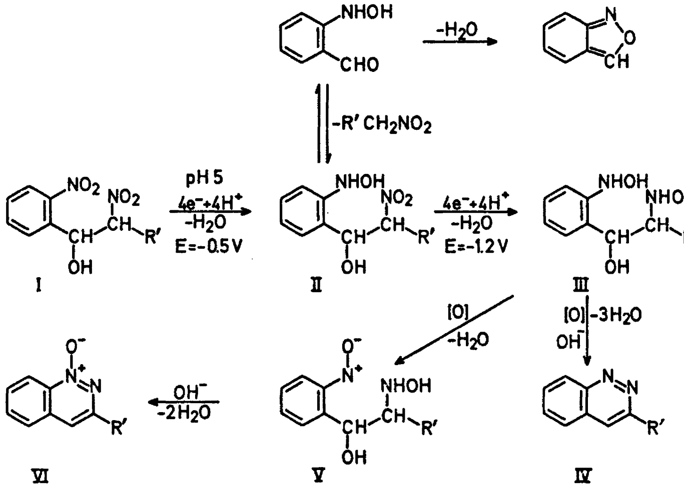
The successive introduction of methyl groups α to the aliphatic nitro group causes a cathodic shift of 70 mV of the half-wave potential of this group; the presence of an α-phenyl group causes an anodic shift of $E_{\frac{1}{2}}$ of the aliphatic nitro group of 25 mV. The half-wave potentials of the *o*-nitro group of *erythro*-Id and *threo*-Id show a significant difference (50 mV); in the case of *erythro*-Ib and *threo*-Ib the difference is only about 10 mV. This finding probably reflects the preferred conformations of the stereoisomeric dinitroalcohols, but a detailed conformation analysis is needed before a definite conclusion can be drawn concerning the origin of this stereochemical effect.

Table 2. Half-wave potentials of *o*-nitro-α-(1-nitroalkyl/aralkyl)benzyl alcohols I in 40 % ethanolic acetate buffer at pH 5.

Compound	$-E_{\frac{1}{2}}$ (1.)	$-E_{\frac{1}{2}}$ (2.)
Ia	0.53	0.85
erythro-Ib	0.54	0.92
threo-Ib	0.55	0.91
Ic	0.57	0.98
erythro-Id	0.47	0.83
threo-Id	0.52	0.82

Preparation of cinnolines. Controlled potential reduction at 0 °C of *erythro*-Ib in an acetate buffer containing 25 % ethanol at a mercury electrode at the potential of the second wave (−1.20 V *vs.* SCE) consumed 8 F/mol; after the reduction the solution was made alkaline and was allowed to stand over night in contact with air before further work-up.

Besides the main product, 3-methylcinnoline, which was isolated after chromatography in 59 % yield, some anthranil could be detected by NMR-spectroscopy of the crude reaction mixture. From the reduction of *threo*-Id at −0.95 V *vs.* SCE was isolated, after a similar work-up, 3-phenylcinnoline and some 3-phenylcinnoline-1-*N*-oxide; anthranil was also here detected in the crude reaction mixture in a yield of 5−10 %. These results are rationalized in Scheme 2.



Scheme 2.

Table 3. Polarographically determined yields of cinnolines (IV) and cinnoline 1-*N*-oxides (VI) from the reduction of *o*-nitro-α-(1-nitroalkyl/aralkyl)benzyl alcohols I in 25 % ethanolic acetate buffer at pH 5.

Compound	$-E$(V *vs.* SCE)	Yield % IV	VI
Ia	1.20	51	0
erythro-Ib	1.20	56 – 63	0
threo-Ib	1.20	67	0
erythro-Id	0.95	49	20
threo-Id	0.95	47	16

In Table 3 are given polarographically determined yields of the cinnolines and the *N*-oxides from a series of runs at pH 5 and 0 – 5 °C, followed by the standard work-up.

Anthranil is a reduction product of *o*-nitrobenzaldehyde. The tendency of a reversal of the Henry addition is low for I, but probably higher for II, as the anthranil formation would remove the *o*-hydroxylaminobenzaldehyde from the equilibrium and thereby favour the cleavage.

This is in accordance with the fact that higher temperatures cause higher yield of anthranil and lower yield of cinnolines. Furthermore, reduction at the potential of the first wave followed by a reduction at the potential of the second wave similarily gives a higher yield of anthranil and a lower one of cinnoline. This substantiates the polarographic results that the first wave is caused by the reduction of the "aromatic" nitro group.

The reduction of the aromatic nitro group may also facilitate the loss of water from II with the formation of an *o*-hydroxylaminonitrostyrene. A formation of such a compound, followed by its reduction and further reactions, may help to explain why the yield of cinnoline never exceeds 65 %. The dehydration of II may also explain why an attempt to suppress the reversal of the Henry addition by conducting the reduction in N sulfuric acid was not successful (yield of 3-methylcinnoline 21 %).

The formation of the cinnoline-1-*N*-oxides is readily explained by an air-oxidation of a hydroxylamino group to a nitroso group followed by a condensation with the other hydroxylamino group to an azoxy compound; aromatization occurs then by loss of the hydroxyl group as water.

Whereas the reaction mechanisms leading to the by-products, anthranil and the cinnoline-*N*-oxides, seem well established, this is not so for the main reaction, Formally, loss of 3 mol of water from III would lead to a cinnoline; any reaction mechanism must explain the following findings.

(a) The ring closure does not proceed at a measurable rate in the absence of oxygen. III is stable in solution under nitrogen, even at high pH; this is important for the synthesis, otherwise the cinnoline formed during the electrolysis would be reduced in preference to the starting material.

(b) In the presence of oxygen the condensation takes place; it goes faster at high pH, but the yield of cinnoline is the same whether the condensation takes place at pH 1 or 12.

(c) The oxidation state of III and IV is the same; any initial oxidation by oxygen in the beginning of the reaction sequence must be followed by a corresponding reduction later in the reaction.

(d) Additions of oxidation agents, such as cupric ions, hexacyanoferrate, or dinitrogen tetroxide, which are recognized as one-electron oxidation reagents, did not increase the yield of cyclized products, although it increased the formation of *N*-oxide at the expense of the cinnoline.

One could assume that the initial step was a one-electron oxidation of III, followed by formation of a nitrogen-nitrogen bond and successive loss of 3 mol of water. The energy gained by the aromatization may make it possible for the radical to oxidize (abstract an electron from) another molecule of III. It has, however, not been possible to obtain experimental verification of this or any other hypothesis.

CONCLUSION

Despite the fact that yields are not quantitative, the ease of preparing the starting materials and conducting the reduction without isolation of intermediates, makes the cinnolines a more accessible class of compounds than hitherto. From a synthetic point of view, it is a further advantage that the tedious separation of the stereoisomeric dinitroalcohols I is superfluous as judged from Table 3.

A better understanding of the critical cyclization step might possibly result in even better yields than we have been able to obtain. On the other hand, if the loss is exclusively caused by a cleavage or loss of water from II, the chance of increasing the yields of cinnolines seems not very promising; possibly reduction at low temperatures may be an advantage.

EXPERIMENTAL

The equipment used for polarography and electrolysis at controlled potential was a recording polarograph P04 (Radiometer, Copenhagen) and a fully transistorized potentiostat (Tage Juul Electronics, Copenhagen) respectively. NMR spectra were obtained with a Varian A-60 spectrometer. Mass spectra were taken on a CEC/MS-21-104 mass spectrometer. M.p's were determined with a Mettler FP-instrument.

General procedure for the preparation of the o-*nitro-α-(1-nitroalkyl/aralkyl)benzyl alcohols (I).* To a stirred solution of *o*-nitrobenzaldehyde (7.55 g, 0.05 mol) and the nitroalkane (0.1 mol) in benzene (25 ml) was added triethylamine (300 μl, 2 mmol). The reaction mixture was kept below 25 °C with external cooling and was then allowed to stand at room temperature over-night. The reaction mixture was diluted with further 100 ml benzene and was extracted with portions of saturated sodium hydrogensulfite solutions (3 x 50 ml) to remove the base catalyst, unreacted aldehyde and coloured impurities. The benzene layer was dried over calcium sulfate and the benzene removed *in vacuo* together with excess nitroalkane.

Deviation from the general procedure. Erythro- and *threo*-Id were for practical reasons prepared from *o*-nitrobenzaldehyde and phenylnitromethane in the molar ratio 2:1. The excess of aldehyde was again removed by extractions with saturated sodium hydrogensulfite solutions (3 x 100 ml) as above.

Separation of the stereoisomeric dinitroalcohols. erythro- and *threo*-Ib and Id, respectively, were separated by partition chromatography on Merck Silica 40. The eluent was prepared by shaking chloroform (1.5 l) with a mixture of methanol (50 ml), 80 % acetic acid (4 ml) and water (150 ml). The silica was deactivated with a small amount of the water phase (4 % by weight). In the case of Id unreacted phenylnitromethane was eluted before the stereoisomeric dinitroalcohols. Typically, crude Id (1.48 g) by partition chromatography as described above (column 16 x 3 cm) yields phenylnitromethane (261 mg), *erythro*-Id (278 mg) and *threo*-Id (741 mg) by elution with 750 ml of the developing solvent.

Characterisation of the dinitroalcohols (I): o-*Nitro-α-(nitromethyl)benzyl alcohol (Ia)* was prepared according to the general procedure in 85 % yield. Recrystallization from benzene/cyclohexane gave m.p. 57.1 °C (lit.[12] 59.5 – 60 °C).

(±)-erythro-o-*Nitro-α-(1-nitroethyl)benzyl alcohol* (erythro-*Ib*) was obtained in 40 % yield by the general procedure as a 1:1 mixture (overall yield 80 %) with the (±)-*threo*-isomer, from which it was separated either by repeated crystallization from benzene or by column chromatography. M.p. 94.5 °C (lit.[12] 92 – 93 °C).

(±)-threo-o-*Nitro-α-(1-nitroethyl)benzyl alcohol (*threo-*Ib)* was separated from the *erythro*-Ib isomer by column chromatography. Light orange oil. (Found: C 47.65; H 4.7; N 12.32. Calc. for $C_9H_{10}N_2O_5$ (226.19): C 47.79; H 4.5; N 12.39).

o-*Nitro-α-(1-nitroisopropyl)benzyl alcohol (Ic)* was prepared according to the general procedure in 68 % yield as a slowly crystallizing orange oil. Recrystallized from lukewarm benzene/cyclohexane. M.p. 54.2 – 56.3 °C. (Found: C 49.92; H 5.2; N 11.59. Calc. for $C_{10}H_{12}N_2O_5$ (240.21): C 50.00; H 5.1; N 11.66).

(±)-erythro-o-*Nitro-α-(1-nitrobenzyl)benzyl alcohol (*erythro-*Id)* was isolated in 16 % yield from the *threo*-isomer and unreacted phenylnitromethane by column chromatography. Recrystallized from benzene. M.p. 115 – 116 °C. (Found: C 58.44; H 4.3; N 9.72. Calc. for $C_{14}H_{12}N_2O_5$ (288.25): C 58.33; H 4.2; N 9.72). ^1H NMR (C_6H_6):* δ 2.38 (1 H, s, O*H*), 5.81 (1 H, d, H^b, J_{ab} 4.5 Hz), 6.09 (1 H, d H^a), 6.5 – 7.7 (9 H, m, arom. H). (DMSO-d_6): δ 6.13 (1 H, d, H^b, J_{ab} 5.5 Hz), 6.31 (1 H, d, H^a), 6.60 (1 H, s, O*H*), 7.2 – 8.2 (9 H, m, arom. H).

(±)-threo-o-*Nitro-α-(1-nitrobenzyl)benzyl alcohol (*threo-*Id)* was obtained in 32 % yield as a light orange oil, which crystallized after standing at room temperature for three months. The crystals were washed with benzene/cyclohexane 2:1. M.p. 81 – 83 °C. (Found: C 58.36; H 4.5; N 9.37. Calc. for $C_{14}H_{12}N_2O_5$ (288.25): C 58.33; H 4.5; N 9.72). ^1H NMR (C_3D_6): δ 3.07 (1 H, s, O*H*), 5.77 (1 H, d, H^b, J_{ab} 9.0 Hz), 6.34 (1 H, d, H^a), 6.5 – 7.4 (9 H, m, arom. H). (DMSO-d_6): δ 6.16 (2 H, s, $H^a + H^b$), 6.84 (1 H, s, O*H*), 7.2 – 8.0 (9 H, m, arom. H).

(±)-threo-α-*(1-Nitrobenzyl)benzyl alcohol* was prepared according to the procedure of Bordwell and Garbisch [7] and recrystallized from benzene/cyclohexane. M.p. 103 – 104 °C (lit.[7] 103.5 – 104 °C). ^1H NMR ($CDCl_3$): δ 3.05 (1 H, s, O*H*), 5.51 (1 H, d, H^a, J_{ab} 9.5 Hz), 5.63 (1 H, d, H^b), 7.1 – 7.4 (10 H, arom. H). (C_6D_6): δ 2.51 (1 H, d, O*H*, J_{aOH} 3.5 Hz), 5.39 (1 H, dd, H^a, J_{ab} 10 Hz), 5.57 (1 H, d, H^b), 6.8 – 7.3 (10 H, arom. H). (DMSO-d_6): δ 5.59 (1 H, dd, H^a, J_{ab} 10.5 Hz, J_{aOH} 4 Hz), 5.94 (1 H, d, H^b), 6.36 (1 H, d, O*H*), 7.0 – 7.7 (10 H, arom. H).

Analytical determination of yields. The dinitroalcohols (I) (0.5 mmol) were reduced at the selected potential in 25 % aqueous ethanol (150 ml) adjusted to the appropriate pH and kept

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* Proton indices, see Table 1.

under nitrogen at 0 – 5 °C. After complete reduction of the nitro groups (the reaction was followed by polarography directly in the cell) the solution was separated from the mercury. The mercury was further washed with 50 ml ethanol and the combined solution was made slightly alkaline (pH 10 – 12) with solid potassium carbonate and allowed to stand overnight in contact with air. The solution was diluted to 250 ml with water and portions (25 ml) were adjusted with 4 N hydrogen chloride to pH 1 and diluted to 50 ml. Yields were calculated from polarograms of these solutions by comparison with standard curves of the corresponding cinnolines (*cf.* Ref. 10).

Preparative reductions

Reduction of (±)-erythro-o-*nitro-α-(1-nitroethyl)benzyl alcohol (*erythro-*Ib). erythro*-Ib (1.00 g) was reduced at 0 °C at – 1.2 V (SCE, sec. wave) in a 25 % ethanolic acetate buffer adjusted to pH 5. The reduction consumed eight electrons per molecule. The solution was then made alkaline with solid potassium carbonate and was left over-night in the presence of air. The polarographically determined yield of 3-methylcinnoline in this solution was 63 %. The solution was then extracted with portions of methylene chloride (3 × 150 ml). The combined extracts were dried over solid potassium carbonate and the solvent evaporated *in vacuo*. The crude product (515 mg) was purified by column chromatography (2.5 × 19 cm) on alumina (Merck, activity I) by elution with ether-light petroleum (b.p. 60 – 80 °C) 1:1 to yield 3-methylcinnoline (375 mg, 59 %; R_F = 0.18). The compound was identified from its NMR-spectrum (CDCl$_3$): δ 2.90 (3 H, s), 7.57 – 7.93 (4 H, m), 8.32 – 8.60 (1 H, m) and its quantitative conversion to the hydrochloride, m.p. 120 – 122 °C (dec.), which was identical with that of an authentic sample.[13]

TLC-evidence and the NMR-spectrum of the crude product revealed a small admixture (5 – 10 %) of anthranil. Furthermore, the spectrum had broad unresolved signals at δ 6.5 – 7.4 probably due to polymeric materials. By a similar reduction of *erythro*-Ib (2.26 g) conducted at room temperature, there was isolated 115 mg (10 %) anthranil (purified by chromatography on silica gel by elution with the earlier described chloroform-methanol-acetic acid-water system; R_F = 0.40).

Reduction of o-*nitrobenzaldehyde*. *o*-Nitrobenzaldehyde (2.00 g) was reduced at – 0.55 V (SCE, first wave) in acetate buffer containing 25 % ethanol with an electron consumption of 4F per mol. The reduced solution was extracted with methylene chloride, which was dried over calcium sulfate and evaporated *in vacuo* at 10 °C; the yield was 1 g of crude product. As TLC revealed a small admixture of starting material, the product was dissolved in benzene (50 ml) and shaken with a saturated aqueous solution of sodium hydrogensulfite. The benzene layer was dried over calcium sulfate and evaporated *in vacuo* to yield anthranil (803 mg, 51 %). ^{1}H NMR (CDCl$_3$): δ 6.77 – 7.80 (4 H, m), 9.13 (1 H, d, 1.1 Hz). MS (70 eV) *m/e* (% I): 119 (M^+, 88), 93 (7), 92 (100), 91 (38), 90 (8), 65 (22), 64 (84), 63 (60) (*cf.* Ref. 1).

Reduction of (±)-threo-o-*nitro-α-(1-nitrobenzyl)benzyl alcohol (*threo-*Id). threo*-Id (0.50 g) was reduced at – 0.95 V (SCE, sec. wave). The reduction consumed approximately eight electrons per molecule. The solution was made alkaline with potassium carbonate and left overnight in contact with air. A white precipitate was filtered off and the solution was further extracted with methylene chloride (3 × 150 ml). After drying over potassium carbonate the solvent was removed and the solid residue combined with the precipitate and subjected to column chromatography on alumina (activity I) by elution with ether-light petroleum (b.p. 60 – 80 %°C) 1:1. By this procedure were isolated 3-phenylcinnoline (168 mg, 47 %; R_F = 0.39), m.p. 118 – 119 °C (lit.[3] 119 °C) and 3-phenylcinnoline 1-*N*-oxide (85 mg, 22 %; R_F = 0.22), m.p. 134 – 136 °C after washing with a little cold methanol (lit.[14] 138 – 139 °C). MS (70 eV) *m/e* (% I): 223 (15), 222 ($M^{+\cdot}$, 100), 206 (17), 178 (28), 176 (12), 165 (10), 119 (13), 97 (10), 92 (60), 91 (37), 89 (26), 83 (13), 77 (22), 76 (20), 71 (12), 69 (22), 64 (20), 63 (24). Before 3-phenylcinnoline 98 mg was eluted, which according to the NMR-spectrum contained anthranil and probably *o*-hydroxylaminobenzaldehyde.

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