

ELECTRON-TRANSFER REACTIONS OF CROSSLINKED POLY(1-PYRIDINIOMETHYL)STYRENE CHLORIDE*

2. REDUCTION OF NITRO-COMPOUNDS

NI Yushan (倪玉山), SHAO Yunglin (邵永林) and XU Jiping (徐纪平)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun)

ABSTRACT

Continuing the study of electron transfer reactions of polypyridiniomethylstyrene chloride (PSPyCl), the reduction of nitro-compounds by the PSPyCl-Zn system was investigated. In general azoxy compounds were obtained as chief intermediate product of reduction. Reduction of nitrobenzo-15-crown-5 and its homologues give a new class of *bis*-crown ether compounds — azoxy-bis-benzocrown ethers. Azoxybisbenzocrown ethers undergo photoinduced *trans*-*cis* isomerization, which is reversible on irradiation with UV and on storage in darkness, similar to the case of azobiscrown ethers. Investigation of solvent extraction of various cations by azobiscrown ether isomers shows that *cis*-azoxybisbenzo-15-crown-5 exhibit good selectivity toward Nd³⁺ from other rare earth cations.

In a previous paper the reduction of quinones by the electron-transfer reaction of cross-linked poly(1-pyridiniomethyl)styrene chloride (I) in presence of Zn powder was reported^[1]. Reduction of nitrobenzene was also examined briefly. In this paper further study of the reduction of nitrocompounds is presented.

The reduction of nitrocompounds is rather complicated. The composition of reduction product is influenced by a lot of factors such as reduction media, reducing power of reducing agent used, structure of the nitrocompounds under reduction etc.

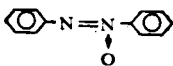
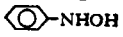
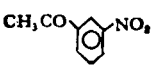
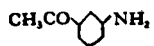
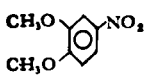
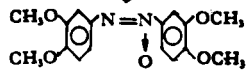
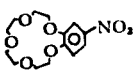
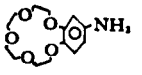
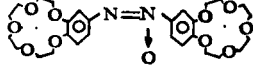
Analysis of resin I gives Cl: 11.25%, N: 4.92%, which corresponds to a content of 3.2 meq. functional pyridium group per gram resin.

Identified reduction products of some nitrocompounds using I as electron transfer agent in the presence of Zn powder are listed in Table 1.

It can be seen from Table 1 that almost all nitrocompounds give azoxy compounds as intermediate product of reduction. The yield of azoxycompounds depends on the ratio of I to nitrocompounds. In the case of nitrobenzene the results of reduction are shown in Table 2 as an example.

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Table 1 Reduction products of some nitrocompounds by system (I-Zn)

Substrate	Products	Yield (%)	Identified by
	 	28.2 11.1	mp, IR, MS mp, IR, MS
		11.3	mp, IR, MS
		25.5	mp, IR, MS
		27.2	mp, IR, MS
		22.6	mp, MS
		48.0	IR, MS
		24.2	IR, MS element analysis
	reduction products not detected		MS

Reactions were conducted at 22–23°C for 24 h.

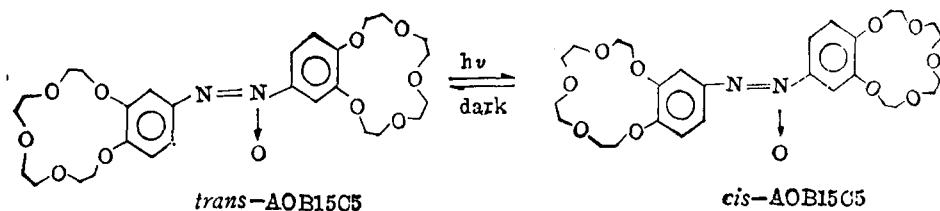
Table 2 Change in composition of reduction products of nitrobenzene at different molar ratio of I/NB

Molar ratio I / NB	4:1	1:1	1:6
N-hydroxyaniline	11.1%	12.9%	30.1%
Azoxybenzene	28.2%	5.4%	2.9%

In the reduction products of 4'-nitro-benzo-15-crown-5 (NB15C5), two compounds have been identified: 4'-amino-benzo-15-crown-5 (AB15C5) and azoxy-bis-benzo-15-crown-5 (AOB15C5). Monitoring the process of reduction with UV-spectra has shown that the amount of AB15C5 produced increases with increasing molar ratio of I/NB15C5, while the yield of AOB15C5 increases with decreasing molar ratio of I/NB15C5. The yield of AOB15C5 is 24.2% and 27.8% at molar ratio of 4:1 and 1:1 respectively.

The yield of AB15C5 can be raised up to 74.0% (crude product) when the reaction is carried out at 60°C for 10 h with a molar ratio of 4:1. It may be mentioned that AB15C5 was usually obtained by catalytic hydrogenation under 25–35 psi hydrogen pressure in presence of Pd catalyst^[2]. It is convincible that reduction of NB15C5 may lead to different products under different conditions^[3–4]. But so far as we know, azoxy-bis-benzo-15-crown-5 is a new biscrown compound obtained from the reduction of 4'-nitrobenzo-15-crown-5 in fairly good yield.

AOB15C5 has similar properties to azo-bis-benzo-15-crown-5 in some aspects. Both exist in *trans*- and *cis*-isomers, and *trans*-AOB15C5 can also undergo isomerization to *cis*-form by UV irradiation from a high pressure Hg lamp, and the reverse process takes place on storage in darkness.



The solvent extraction of rare earth metal cations and alkali metal cations by AOB15C5 isomers was also investigated, and the results indicate that *cis*-AOB15C5 shows good selectivity toward Nd^{3+} cation^[5].

It is interesting to point out that only nitro-group is reduced by system I/Zn while carbonyl group remains untouched when both nitro- and carbonyl groups exist in the same molecule, as in the case of *m*-nitroacetophenone (Table 1).

EXPERIMENTAL

Reduction of *m*-nitroacetophenone

To a solution of 0.171 g *m*-nitroacetophenone in 15 ml of mixed solvent (1,4-dioxane/water, vol. ratio 9:1) 1.26 g of I and 1.32 g of zinc powder were added. The mixture was stirred magnetically at room temperature for 24 h. After filtration and extraction of the residue with CHCl_3 , the combined solution was concentrated and the components separated on an Al_2O_3 column ($\phi 8 \times 110$ mm), 0.038 g of *m*-aminoacetophenone and 0.037 g of 3,3'-diacetyl-azoxybenzene were obtained, the yields were 27.2% and 25.5% respectively.

Reduction of 4-nitroveratrole

To a solution of 0.183 g 4-nitroveratrole in 15 ml of mixed solvent 1.26 g of I and 1.32 g of zinc powder were added. The operation was the same as above. The residue was separated by centrifugal thin layer chromatography (eluted by mixed solvent: CHCl_3 /petroleum ether 9:1 v/v) 0.036 g of 3,3', 4,4'-tetramethoxyazoxybenzene was obtained (22.6% yield).

Reduction of 4'-nitrobenzo-15-crown-5

To a solution of 0.315 g of NB15C5 in 15 ml mixed solvent 1.26 g of I and 1.32 g of zinc powder were added. After stirring at room temperature for 24 h the residue was filtrated and extracted with chloroform for 2 h. The combined solution was concentrated to a dark-brown viscous mass and taken up in 5 ml of acetone, and a yellow solid was precipitated. After filtration (filtrate was reserved) and drying, 0.070 g of azoxybisbenzo-15-crown-5 was obtained (24.2% yield). m.p. 159–160°C, elemental analysis: C 57.08, H 6.57, N 4.65; calc, for $\text{C}_{28}\text{H}_{38}\text{O}_{11}\text{N}_2$: C 58.13, H 6.57, N 4.84. $\text{MS}^+ = 578$ (m/e).

Evaporation of the filtrate gave 4-aminobenzo-15-crown-5 as identified by MS ($\text{MS}^+ = 283 \text{ m/e}$).

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