

A Simple Synthesis of 2,2'-Azobis[(15-crown-5)- eno [g] quinoxaline]

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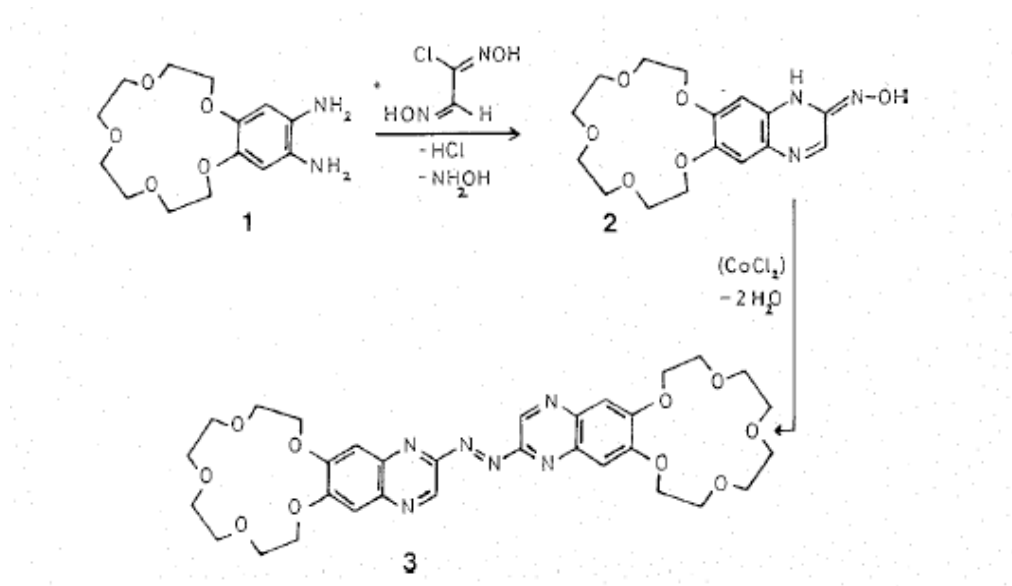
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Einfache Synthese von 2,2'-Azobis[(15-krone-5)eno[g]chinoxalin]

Die Umsetzung von 2,3-Diaminobenzo-15-krone-5 (1) mit *s-trans*-Chlorethandial-dioxim in Ethanol liefert das 2(1H)-(15-Krone-5)eno[g]chinoxalinon-oxim (2), das durch Templat-Effekt von Co²⁺ in das 2,2'-AzobisE(15-krone-5)eno[g]chinoxalin (3) übergeführt wird.

Bis(crown ethers) are proven to be extremely powerful extracting agents for alkali metal salts. In this regard, the photoresponsive bis(crown ethers) which contain an azo group as a photoantenna to capture photons have been investigated recently for the photocontrol of their complexation with alkali metal ions^{1,2}. On the other hand, we have reported the conversion of 2(1H)-quinoxalinone oxime into 2,2'-azobis(quinoxaline) by the template effect of cobalt and nickel ions^{3,4}.

The object of the present study is to synthesize a new compound which simultaneously contains both azobis(quinoxaline) and crown ether groups by making use of the template effect of cobalt(II) ions (scheme).



2(1H)-(15-Crown-5)eno[g]quinoxalinone oxime (2) was synthesized from *s-trans*-chloro-ethanedial dioxime and 2,3-diaminobenzo-15-crown-5 (1) which was obtained from benzo-15-crown-5 *via* nitro-, amino-, (acetyl amino)-, (acetyl amino)nitro-, aminonitrobenzo-15-crown-5 as previously reported⁵⁻⁷. The formation of a quinoxaline ring probably directed this cyclization reaction.

When a solution of 2 and cobalt(II) chloride in absolute ethanol was heated at 60°C for 4 h, 2,2'-azobis[(15-crown-5)eno[g]quinoxaline (3) was isolated as a reddish brown precipitate. Though the absolute mechanism of this reaction is not known, we might expect the formation of a complex with a deprotonated 2 and cobalt ion in the first step, since we have isolated a dark purple insoluble product corresponding to C₁₆H₂₀ClCoN₃O₆ in the case of more concentrated reaction mixtures and excess cobalt(II) ions. The highest yield was obtained when the initial ratio of the reactants was 2(2): 1(Co), but the reaction still took place with much smaller rates even when the ratio was 10:1.

The almost perfectly planar structure of trms-2,2'-azobis(quinoxaline) determined by single crystal analysis⁴) is not expected in 3 because of the bulky crown ether groups attached to the aromatic rings, but 3 is also in (trans-structure as deduced from the electronic spectrum.

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Experimental

2(1H)-(15-Crown-5)enof[g]quinoxalinone Oxime (2): To the solution of 2.98 g 2,3-di-aminobenzo-15-crown-5 (1) (10 mmol) in absol. ethanol (100 ml) under stirring at room temperature was added a solution of s-trans-chloroethanedial dioxime (1.23 g, 10 mmol) in absol. ethanol (30 ml). The colour of the solution gradually turned to bright yellow and the precipitation started. The stirring was continued for 1 h. The yellow precipitate was filtered off, washed with ethanol and then with diethyl ether and dried in vacuo. Yield 2.60 g (74%), m.p. 184°C (dec.). - IR (KBr): 3370 (NH), 3170 (OH), 3035 (CH_{arom.}), 2920, 2860 (CH_{aliph.}), 1645 (C = N), 1405 (OH), 1265- 1225 (Ar-O-C), 1190-1130 (C-O-C), 955 (N-O). - UV-VIS (ethanol): λ_{max} (ϵ) = 380 (19690), 255 (69700), 218 nm (61100). - ¹H-NMR ([D₆]DMSO): δ = 3.80 (s; 8H, C-O-CH₂), 3.85 (s; 4H, Ar-O-C-CH₂), 4.1 (s; 4H, Ar-O-CH₂), 6.9 (s; 1 H, Ar-H), 7.0 (s; 1 H, Ar-H), 7.75 (s; 1 H, N = CH), 9.95 (s; 1H, NH), 10.10 (s; 1 H, OH). - ¹³C NMR ([D₆]DMSO): δ = 68.2-70.6 (8 peaks), 99.1, 113.5, 128.2, 143.0, 147.3, 150.1. - MS (70 eV): m/z = 351 (19%, M⁺).

C₁₆H₂₁N₃O₆ (351.4) Calc. C 54.70 H 6.02 N 11.97 Found C 54.08 H 6.19 N 11.97

2,2'-Azobis[(15-crown-5)enofgquinoxaline] (3): To a solution of 2 (0.35 g, 1.0 mmol) in absol. ethanol (50 ml) was added a solution of cobalt(II) chloride hexahydrate (0.12 g, 0.5 mmol) in ethanol (10 ml). The mixture was stirred at 60°C under nitrogen atmosphere for 2 h. The colour of the solution turned to dark red from the initial blue colour. A reddish brown precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with ethanol and then with diethyl ether and dried in vacuo. Yield 0.22 g (67%), m.p. 214°C. - IR (KBr): 3055 (CH_{aromj}), 2920, 2850 (CH_{aliph}), 1610 (C = N), 1290-1235 (Ar-O-C), 1160-1120 (C-O-C). - UV-VIS (chloroform): λ_{max} (ϵ) = 424 (27600), 286 (20650), 240 nm (13300). - ¹H NMR ([D₆]DMSO): δ = 3.67 (s, 16 H, C-O-CH₂), 3.89 (s, 8H, Ar-O-C-CH₂), 4.35 (s, 8H, Ar-O-CH₂), 7.44 (s, 2H, Ar- H), 7.50 (s, 2H, Ar-H), 9.22 (s, 2H, N=CH). - MS (70 eV): m/z = 668 (4%, [M + 2]⁺), 654 (100, M - 12).

C₃₂H₃₈N₆O₁₀ (666.7) Calc. C 57.66 H 5.71 N 12.61 Found C 57.23 H 5.77 N 12.88