Formation of Acyclic *cis*-Azobenzene without Light

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Synopsis. Reduction mixture of bis(4-nitrobenzyl) ether contained a considerable amount of *cis*-4,4′-dimethylazobenzene.

Although several chemical syntheses of *trans*-azobenzene derivatives are known,[1] chemical syntheses of *cis* isomers are known only in the case of cyclic azobenzene derivatives.[2] The only method to synthesize acyclic *cis*-azobenzene derivatives ever known is a photochemical one, namely, exposing the corresponding *trans*-azobenzene derivatives to UV light.[3] This is probably due to the fact that the intermediates in the chemical formations of azo linkages energetically favor *trans* conformations about the N–N bonds. In this note we describe the one-pot chemical formation of *cis*-4,4′-dimethylazobenzene, **3**, without using light.

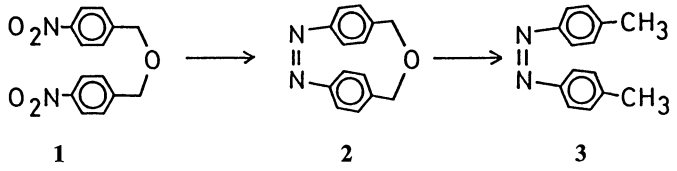
Bis(4-nitrobenzyl) ether, **1**, was reduced with $LiAlH_4$ in dry THF by a high-dilution method. It was found by TLC that the reaction mixture contained several orange products. The mixture was then separated by column chromatography. Two main orange compounds which were eluted together during the early stage of chromatography were further separated by preparative GPC and crystallized by slow evaporation of the solvent under atmospheric pressure at room temperature. One of the fractions was identified as being *trans*-4,4′-dimethylazobenzene by comparing the ^{1}H NMR and retention time on reversed-phase HPLC with an authentic sample# which was synthesized by the reduction of 4-nitrotoluene. Identification of the fraction was further confirmed by FD-MS. The detected mass was 210, which corresponds to 4,4′-dimethylazobenzene. The other fraction of the preparative GPC showed two peaks on reversed-phase HPLC after crystallization. This means that the compound in this fraction of GPC is slowly changed to another compound in the dark. On the ^{1}H NMR chart there exist four kinds of doublets (each two peaks of which is coupled) and two kinds of singlets. By a comparison of ^{1}H NMR and the retention time on reversed-phase HPLC with an authentic mixture prepared by the UV irradiation of *trans*-4,4′-dimethylazobenzene in solvent, the second isolated fraction was identified as being a mixture of *trans*- and *cis*-4,4′-dimethylazobenzene.

Since we performed the entire process under yellow light (<500 nm), it is certain that *cis*-4,4′-dimethylazobenzene is formed chemically, not photochemically. This interesting phenomenon is explained as below (scheme). Bis(4-nitrobenzyl) ether was first reduced to form 2-oxa-10,11-diaza[3.2]paracyclophan-10-ene, **2** in which the azo linkage is fixed to the *cis* form due to a ring restriction. The cyclophane is destabilized by ring strain and is thus very easily further reduced to form an acyclic azobenzene derivative, **3**, while maintaining the azo configuration in the *cis* form. Another possible route, in which the ether linkage of **1** is first decomposed to form 4-nitrotoluene and then converted to **3**, is excluded by the following observation. A reduction of 4-nitrotoluene under similar conditions did not produce *cis*-4,4′-dimethylazobenzene, but produced *trans*-4,4′-dimethylazobenzene only.

This proposed reaction process to form the *cis*-azobenzene derivative is also interesting fields involving the synthesis of cyclophanes which contain hetero atoms. The synthesis of 10,11-diaza[3.2]paracyclophane-10-enes has not yet succeeded, in spite of the intensive efforts by Funke and Grützmacher.[4] Although we have not yet isolated 10,11-diaza[3.2]paracyclophane-10-enes, we believe that 1,3-bis(4-nitrophenyl)propane will be stably converted to 10,11-diaza[3.2]paracyclophan-10-ene under the same reduction conditions as described in this study.

Experimental

Synthesis of Bis(4-nitrobenzyl) Ether, 1: **1** was synthesized by a bimolecular condensation of 4-nitrobenzyl alcohol, **4**. 6 ml of concd H_2SO_4 was added to 25 g of **4** in 150 ml of benzene. The solution was heated under reflux for 4 h. After that, H_2SO_4 was further added until **4** completely disappeared. After 25 h the solution was cooled to room temperature and washed four times with 100 ml (each) of water. A small portion of **1** appeared as a white solid two or three days after removing the benzene from the solution by evaporation. Additional **1** appeared after removing (4-nitrophenyl)-



1 **2** **3**

Scheme 1.

#^{1}H NMR (270 MHz) *trans*-4,4-dimethylazobenzene ($CDCl_3$) δ=2.43 (s, 6H), 7.30 (d, J=8.2 Hz, 4H, Ar), 7.81 (d, J=8.2 Hz, 4H, Ar); *cis*-4,4′-dimethylazobenzene ($CDCl_3$) δ=2.30 (s, $-CH_3$), 6.77 (d, J=7.2 Hz, 4H, Ar), 7.05 (d, J=7.2 Hz, 4H, Ar).

phenylmethane[5] from the remaining solution by distillation. The product was combined and recrystallized from ethanol. 3.82 g (16.2%), mp 97—98 °C (lit,[6] 97—98 °C), ^{1}H NMR ($CDCl_3$) δ=4.72 (s, 4H, CH_2OCH_2), 7.55 (d, 4H, Ar), 8.24 (d, 4H, Ar).

Reduction of 1: A solution of 5.0 g of **1** in 100 ml of dry THF was added dropwise for 3 h to a suspension of 3.4 g of $LiAlH_4$ in 140 ml of dry THF under a nitrogen atmosphere. After 20 h of stirring, a small amount of water was carefully added to the reaction mixture in order to destroy the remaining any $LiAlH_4$. O_2 was then passed through the reaction mixture for 4.5 h in order to oxidize any hydrazo compounds to the corresponding azo compounds. The solid was filtered off and the filtrate evaporated. The residue was extracted by chloroform. A condensed chloroform solution was transferred to a silica gel column and eluted with hexane–chloroform (1 : 1 v/v). The first eluent was further purified by preparative GPC (Waters, ULTRASTYRAGEL 500 Å+100 Å/chloroform). *cis*- and *trans*-4,4′-Dimethylazobenzene was eluted at retention volumes of 95.5 and 99.6 ml, respectively. By slowly evaporating of chloroform parts of the first fraction (8.07 mg, 0.21%) and second fraction (0.196 g, 5.1%) were isolated.

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