

## REACTION OF DIBENZYLAMINES WITH $\pi$ -ACCEPTORS

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**SUMMARY:** Dibenzylamines *la, b* reacted with 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) in aerated dichloroethane under  $\alpha$ -H-atom abstraction and formation of DDQ-H<sub>2</sub>, benzaldehyde and aromatic amines. While Tricyanovinilation product was obtained on reaction with tetracyanoethylene (TCNE).

**Key Words:** Dibenzylamine,  $\pi$ -receptors.

### INTRODUCTION

The reaction of N,N-dimethylamines with tetracyanoethylene (TCNE) and 1,4-benzoquinones has been the subject of several investigations via the formation of charge-transfer (CT) complexes (1-9).

DDQ has been widely used as a powerful dehydrogenating agent synthetic organic chemistry (10-12) and has also been considered as a one electron oxidant (12,13). Asymmetric oxidation of benzylic carbon using DDQ has been reported (14).

The interesting behavior of the N,N-dimethylamine system towards the  $\pi$ -acceptors prompted me to investigate the donor properties of its derivatives, N,N-dibenzylamines featuring two active methylene groups attached to the nitrogen atom *1*. The interaction between DDQ and *1* results in formation of benzaldehyde and the corresponding aromatic amine indicating an interesting anomalous behavior of *1* towards DDQ. The mechanism of formation of the reaction products may be explained as follow; mixing a solution of DDQ in dichloroethane with compounds of *1a, b* in the same solvent results in an initial formation of CT-complex with a characteristic green color, which gradually changed to the anion radical DDQ and cation radical *1* (2). The radical ion pair *2* which in equilibrium with the CT-complex can be represented by the nitrogen cation radical in contact with DDQ anion radical *3* followed by transfer of an  $\alpha$ -proton to DDQ to generate the  $\alpha$ - carbon radical *4* with DDQ-H *5*. Attack of aerial oxygen on the methylene radical *4* giving rise to form the peroxide radical *6*, and on abstraction of hydrogen proton from the source *1* gave *7*. Addition of H<sub>2</sub>O to *7* and elimination of hydrogen peroxide gave the hydroxy compound *8*.

On repeating these steps with the other methylene group gave the dihydroxy compound *9*, which rearranges to yield the products *11* and *12*.

DDQ-H abstracts a hydrogen proton from *8* to give *10*. The structure of the hydroquinone (DDQ-H<sub>2</sub>) *10* was established from the comparison of its IR spectrum and melting point with those of an authentic sample, prepared by reduction of DDQ with sodiumbisulfite in dioxane/iso-propanol mixture. The structures of aromatic amines and benzaldehyde were assigned on the basis of their spectroscopic as well as physical properties.

On the other hand the reaction of TCNE with dibenzylamine *1a* gave the expected tricyanovinilation product *13*, however in case of *1b* stable CT-complexes have been formed which exhibit the characteristic broad absorption band in the visible region (Table 1) and decomposed after 48 hours yielding both reactants on the chromatographic plates (15). The tricyanovinilation *13* was characterized by its usual pink color, attributable to the extended conjugated system. The IR spectrum of *13* shows a sharp absorption band at 2210 cm<sup>-1</sup> characteristic of conjugated C=N group. The molecular formula of compound *13* was evidenced from the elemental analyses as well as the mass spectrum.

### EXPERIMENTAL

2,3-Dicyano-5,6 - dichloro-1,4-benzoquinone (DDQ, Aldrich) was recrystallized from benzene/chloroform (2:3); tetracyanoethylene (TCNE, Merck) was recrystallized from chlorobenzene and sublimed. The dibenzylamines *1a, b* were prepared according to literature 16. Dichloroethane was purified dried and distilled according to Vogel (17).

The electronic spectra were recorded within a wavelength range 350-1100 nm, using Perkin-Elmer lambda 2 spectrophotometer. All the melting points are uncorrected.

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Table 1:  $\lambda_{\max}$  of the charge-transfer complexes of dibenzylamines *1a*, *b* with both DDQ and TCNE in dichloroethane at room temperature 25°C.

Donor	DDQ $\lambda_{\max}$ (nm)	TCNE $\lambda_{\max}$ (nm)
1a	950.620	800
1b	960.628	864

IR spectra were recorded on a Shimadzu 470 spectrophotometer. Elemental analyses of compound *13* was carried out by Fach. Chemie, Universitat Duisburg (FRG), also the mass spectroscopy was recorded on Varian MAT 311A (EI-mode at 70 eV) in Duisburg.

#### The reaction of dibenzylamines *1a*, *b* with DDQ

To a solution of 0.454 gm (0.002 mol) DDQ in 30 ml abs. dichloroethane, the dibenzylamine (0.001) in 10 ml of abs. dichloroethane was added with stirring at room temperature. Stirring was continued for 48 hours. The reaction mixture was filtered and the precipitate was washed with cold dichloroethane several times until the mother liquor became clear. The filtrate was concentrated and the residue was then chromatographed on thin layer plates using toluene as eluent to give two zones, the first contained compound *11* and the second *12*. The two zones were extracted with acetone and concentrated under vacuum at room temperature. The structures of *11* and *12* were confirmed from their physical properties as well as formation of corresponding 2,4-dinitrophenylhydrazone and diazo compounds respectively. The precipitate recrystallized from ethanol to give DDQ-H<sub>2</sub>.

#### Reaction of dibenzyl aniline *1a* with TCNE

To a solution of 0.256 gm (0.002 mol) TCNE in 30 ml abs. dichloroethane, the dibenzyl aniline *1a* 0.273 gm (0.001 mol) in 10 ml of abs. dichloroethane was added with stirring at room temperature. The reaction's color was gradually changed from green to a pink. The stirring was continued for 48 hours. The reaction mixture was concentrated and the residue was then chromatographed on thin layer plates using cyclohexane/ethyl acetate (5:1) as eluent to give a pink colour zone, which was extracted with acetone. Recrystallization of the product with acetone afforded a pure pink crystals of *13*, yield 86%; m.p.

169-170°C. IR (KBr):  $\nu = 2960 \text{ cm}^{-1}$  (aliph-CH); 2210 (CN); 1600 (Ar-C=C) -MS(70 eV) : m/z (%) = 374 (M<sup>+</sup>, 100); 348 (20); 297 (18); 283 (95); 206 (34); 178 (35); 152 (25); 126 (11); 92 (43).

C<sub>25</sub>H<sub>18</sub>N<sub>4</sub> (374.445) Calcd C 80.19 H 4.84 N 14.96  
Found C 80.29 H 4.83 N 14.92

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