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ANODIC CYCLIZATION OF DI-2-NAPHTHYLAMINE

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A new compound, 5,12-di-2-naphthyldibenzo[c,j]phenazine, was found to be produced in about 30% yield by anodic oxidation of di-2-naphthylamine in acetonitrile at 0.7 V (*vs.* Ag/Ag$^+$) with a platinum electrode.

The oxidative cyclization of 4,4'-disubstituted diphenylamines to form the corresponding diphenylphenazines has been known to occur both chemically[1)] and electrochemically.[2)] Recently, Berkenkotter and Nelson[3,4)] studied the anodic cyclization of N,N,N'-triphenylphenylene-1,2-diamine (1) and proposed that an intramolecular cyclization of 1-like compounds is the key reaction for producing diphenylphenazines from substituted diphenylamines. For polynuclear secondary amines, however, no report has been published on the anodic cyclization. In the case of di-2-naphthylamine (2), moreover, not the phenazine-type compounds but 1,1'-bis(di-2-naphthylamine) (3) and N,N,N'-tris(2-naphthyl)-naphthylene-1,2-diamine (4) were formed by chemical oxidation using permanganate.[5)] From analogy with 1, 4 is inferred to be the intermediate for producing the phenazine-type compound. Thus, stronger oxidation than the chemical oxidation of 2 seems to give the corresponding phenazine. From a viewpoint of electroorganic synthesis, anodic cyclization of 2 is significant because selection rules[3,4)] which define the structural requirements of diphenylamines for the formation of diphenylphenazines can be extended.

In this communication, we report that a new phenazine-type compound, 5,12-di-2-naphthyldibenzo[c,j]phenazine (5), was formed in a yield of about 30% by anodic oxidation of 2: This indicates that the electrochemical oxidation is useful for synthesizing phenazine-type compounds.

2 was synthesized according to the literature,[6)] and was recrystallized twice from ethanol; mp 172-173 °C (lit. 170-171,[6)] and 172-173[5)] °C). M$^+$, 269 (M, 269.3).

Preparative-scale electrolysis of 2 was carried out using a two-compartment cell; anolyte was usually 150 ml in volume. The working (*ca.* 120 cm^2) and the counter electrodes were Pt plates. An Ag/0.01 mol dm^{-3} $AgClO_4$ (MeCN) couple was used as the reference electrode. The details of experimental techniques and apparatuses used were reported elsewhere.[7)]

After exhaustive oxidation at 0.7 V, the solution was concentrated to about

10 ml and 10 ml of water was added to the solution, and then the products were extracted with benzene: The supporting electrolyte ($NaClO_4$) remained in the MeCN-water mixture layer which was completely separated from the benzene layer. In the present paper, one product which obtained in the highest yield among the products is discussed in detail. The product was separated by thin-layer chromatography: After the products were chromatographed with benzene using 1 mm alumina (Wako B-10) layers, a part of the chromatogram was scraped off and the product was eluted with methanol. From 202 mg of 2 (5 mmol dm^{-3} solution), for example, the yield of the product (R_f-value, *ca.* 0.2. mp, 289-290 °C. a brownish red crystal) was about 60 mg (30%).

Preparative-scale Electrolysis. The cyclic voltammogram of 2 showed two anodic peaks at peak potentials (E_p) of 0.56 V (I_a) and 0.86 V (II_a). After controlled-potential electrolysis at 0.7 V, wave I_a diminished and the reduction wave appeared (Fig. 1) at E_p = -0.3 V (I_c), which was due to reduction of protons liberated in the following chemical reaction. During electrolysis, the solution became reddish brown, and the n-values (electrons consumed/molecule of 2) observed were 2.07 ± 0.15 for 1-10 mmol dm^{-3} solution of 2. A major product isolated was confirmed to be 5 by the following data. (i) In the IR spectrum of the product (Fig. 2), the N-H stretching absorption of a secondary aromatic amine at 3400 cm^{-1} for 2 disappeared. The C-N stretching absorption of a secondary aromatic amine at 1310 cm^{-1} for 2 also disappeared, and that of a tertiary aromatic amine was observed at 1410 cm^{-1}, which is somewhat shifted to a larger wavenumber because of the resonance with the aromatic rings. (ii) The mass spectrum of the product exhibited a simple pattern, and the parent ion peak at m/e = 534 and its cleavage are reasonably explained in terms of the structure of 5 (Fig. 3). (iii) The results of the elementary analysis were in good agreement with those calculated for 5. Found: C, 89.7; H, 5.2; N, 5.08%. Calcd for 5: C, 89.9; H, 4.9; N, 5.2%.

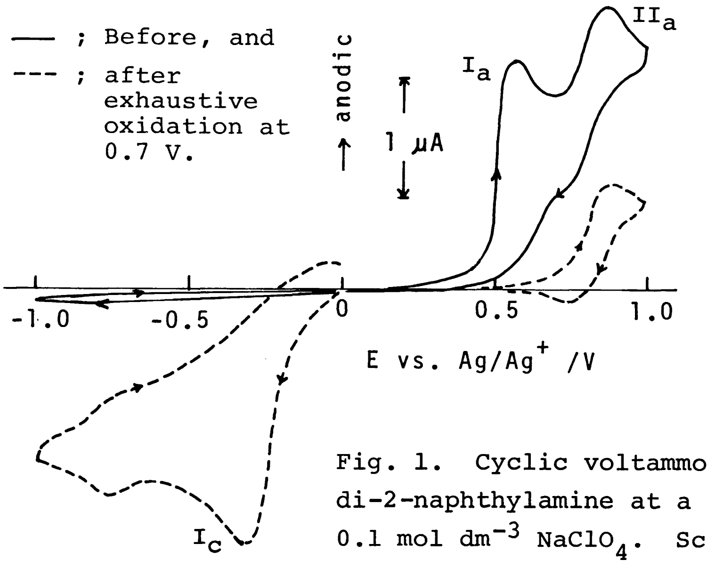


Fig. 1. Cyclic voltammograms of 1 mmol dm^{-3} di-2-naphthylamine at a Pt electrode in MeCN-0.1 mol dm^{-3} $NaClO_4$. Scan rate: 0.2 V s^{-1}. Electrode area: 0.002 cm^2.

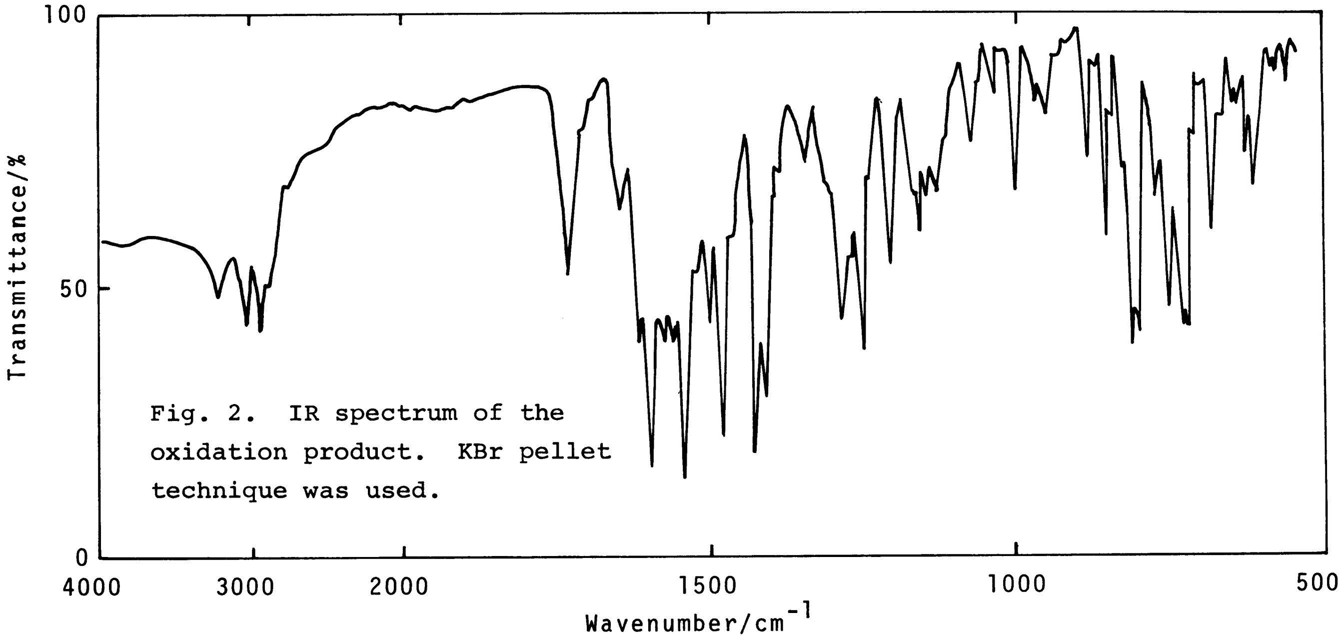


Fig. 2. IR spectrum of the oxidation product. KBr pellet technique was used.

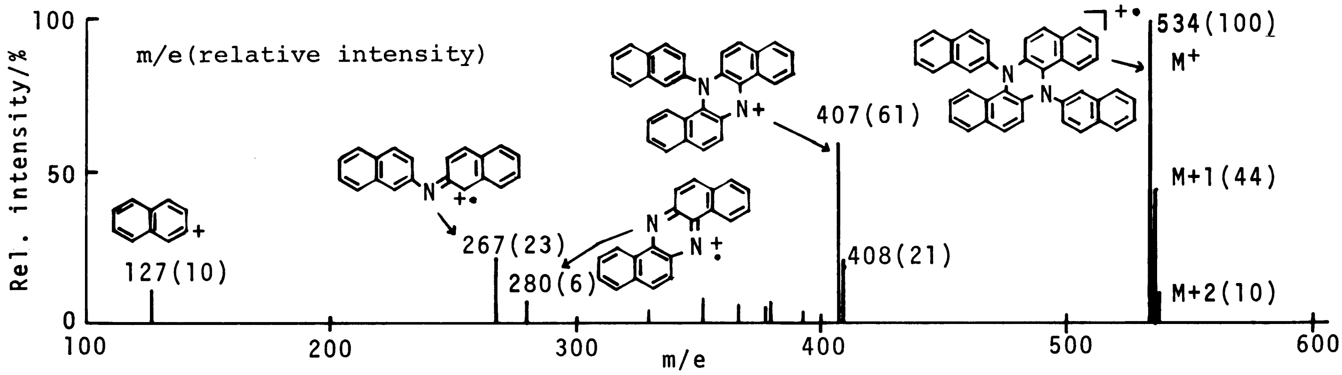
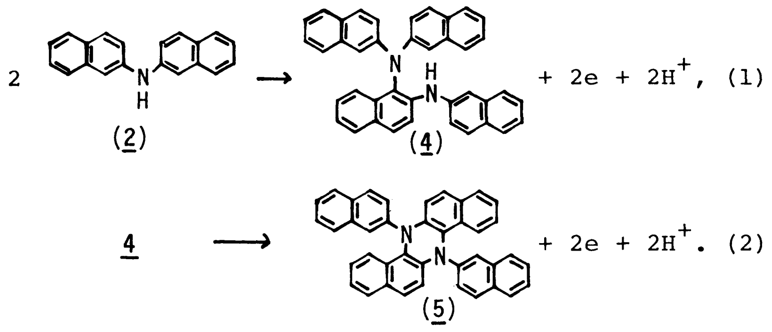


Fig. 3. Mass spectrum of the oxidation product. (75 eV at 210 °C)

(iv) The NMR spectrum (in $CDCl_3$) showed no appreciable peaks, except for those due to aromatic protons. (v) A relatively high melting point (289-290 °C) suggested a stable structure. Thus, we concluded that the anodic cyclization of 2 occurred.

Oxidation Pathway. During electrolysis at 0.7 V, the current did not show an exponential decay with time (Fig. 4): This indicates the presence of a relatively long-lived intermediate in the reactions. The peak current of wave I_C at the end of the electrolysis showed that two protons/molecule of 2 were released in the following chemical reaction. The *n*-value (= 2), the number of released protons (= 2 per molecule of 2), and the shape of the decay curve of the current (Fig. 4) suggest that 5 was formed by the following reactions, which are similar to those proposed for 4,4'-disubstituted diphenylamines, where 4 is a relatively stable intermediate.



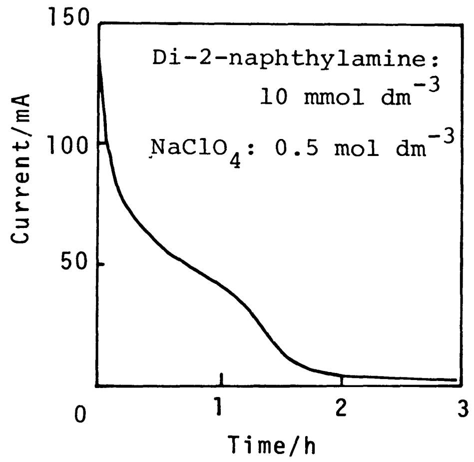


Fig. 4. Current-time curve during oxidation at 0.7 V.

Thus, 5, which was not obtained by chemical oxidation using permanganate,[5)] was produced electrochemically: This suggests that the oxidation ability of permanganate was insufficient for producing 5 under the conditions used in Ref. 5, and the electrochemical oxidation is more preferable technique for synthesizing phenazine-type compounds because the oxidation potential can be changed easily.

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