Tetrahedron Vol. 42, No. 16, pp. 4517 to 4521, 1986
Printed in Great Britain.

0040–4020/86 $3.00+.00

A NOVEL SYNTHESIS OF QUINONE-IMMONIUM DYES

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(*Received in UK* 21 *April* 1986)

Abstract: A new method was invoked to synthesize the colored quinoneimmonium cations from the reactions of DMSO with aromatic amines. The novel feature about this method is the use of DMSO as the methylating agent with a lewis acid such as $TiCl_4$ as a catalyst. This reduced the number of steps traditionally used to prepare these dyes from aromatic amines.

Introduction

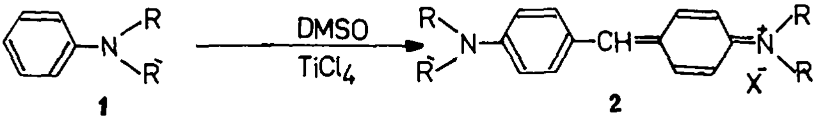
Interest in the colored quinone-immonium dyes is rapidly growing, due to their wide use in copying processes and other practical purposes. Numerous methods have been developed to prepare these dyes, all of which depend on the oxidation of bis(4-N,N-substituted aminophenyl) methanes[1-6]. Arnold and Mentzel have reported that 4,4'-N,N,N',N'-tetramethyldiaminodiphenylmethane can be oxidized with ozone to yield the corresponding blue colored quinone-immonium cation[2,5]. Also, Michler's hydrol was found to give quinone-immonium cation upon oxidation[5]. In 1974, Kast and Baumann[6] reported the preparation of some quinone immonium dyes by the oxidation of bis(4-N,N-R,R'-aminophenyl) methanes ($R=R'=CH_3$ or C_2H_5) under vigorous conditions, using chloranil in the presence of oxygen radical and cobalt complex as a catalyst. It is obvious that the preparation of quinone-immonium dyes involves, as initial stage, the preparation of bis(4-N,N-R,R'-aminophenyl) methanes, which were prepared by different procedures[7-12].

In a recent communication[13], we reported a new one-step method for the preparation of quinone-immonium cation from the reaction of dimethyl-sulfoxide (DMSO) with N,N-dimethylaniline. In order to investigate the generality of this method, we studied the reactions of DMSO with different classes of aromatic amines. In addition, the reaction of N-phenylaza-15-C-5, which is analogeous to N,N-dimethylaniline, with DMSO was explored. This paper reports the general synthetic approach of quinone-immonium dyes from the reaction of DMSO with aromatic amines and their characterization. In addition, the role of the crown ether ring on the reaction is discussed togother with a tentative rationalized mechanism which may account for the course of the reaction.

Results and Discussion

When a mixture of anhydrous DMSO and an aromatic amine 1(a-e) was heated to ca. 150°C in the presence of a lewis acid, a deep-blue to pink colored solution was formed. The produced color is due to the formation of dyes 2(a-e) as shown in Scheme 1.

Scheme 1



1a R = R' = Me
1b R = H; R' = Me
1c R = H; R' = Et
1d R = R' = H
1e N-phenylaza-15-C-5

The color of the resulting dyes is affected by the substituents on the nitrogen atom.

It is worth mentioning that the above reaction does not proceed in the absence of a lewis acid. Thus, the heating of any aromatic amine 1(a-d) with DMSO produces no color, however, the addition of a small quantity of lewis acid such as $FeCl_3$, $Hg(NO_3)_2$, $CuBr_2$ or $TiCl_4$ to the hot solution results in a simultaneous appearance of a blue to pink color. The formation of products 2(a-d) was confirmed by elemental analysis and spectroscopic measurements including UV-Visible, IR, ^{1}H-NMR and MS. The details of these measurements are presented in the experimental part.

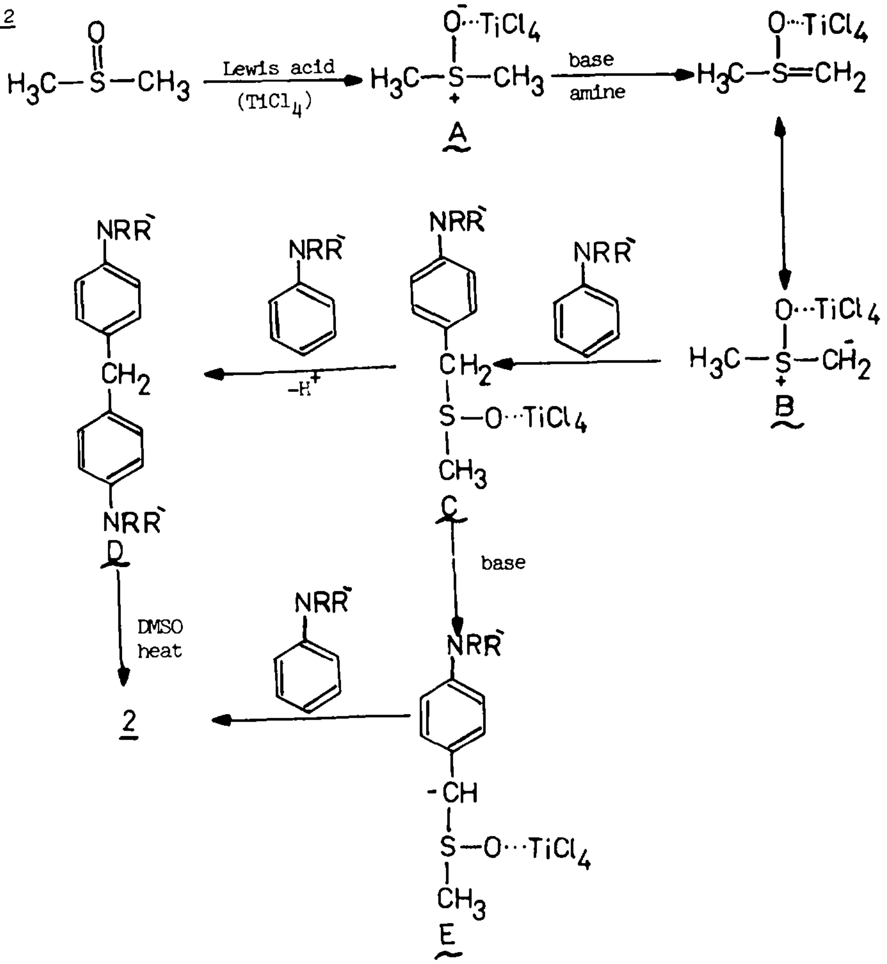
In a comparative study we took N-phenylaza-15-C-5 (1e), which is analogeous to N,N-dimethylaniline, as an aromatic amine to investigate if the crown ether ring has any role on the reaction. We found that compound 1e reacts rapidly with DMSO in the presence of $FeCl_3$ and at a temperature of about 60°C to produce a deep blue color. In another trial, the reaction of 1e with DMSO was conducted without using any lewis acid, a deep blue color appears when the reaction mixture was heated at a temperature of ca. 150°C. The products of the reaction of 1e with DMSO in the presence or absence of the lewis acid are the same as confirmed by spectroscopic measurements.

Mechanism. A possible mechanism which may account for the formation of products 2(a-e) is presented in Scheme 2. We suggest that DMSO reacts with lewis acid to form the sulphonium ion A which will losea proton by the action of the base (amine) to give the nucleophilic species B. This nucleophile makes a nucleophilic substitution on the para position of the armatic amine to produce the intermediate C. One possible reaction for C is to be attacked by another molecule of the amine, which will give bis(4-N-R,R'-aminophenyl) methane, D. Compound D is then oxidized by DMSO under the experimental conditions used to give products 2(a-e). The latter assumption is proved to be correct by showing that bis(4N,N-dimethyl minophenyl) methane, can be oxidized with DMSO at high temperature to give the blue-colored product. Another possible path is that C might produce, in the presence of the amine, the nucleophilic species E which attackes another amine molecule to yield the resulting products. However, it is very difficult to differentiate between these two possible paths.

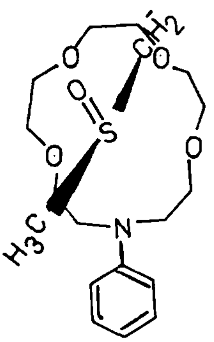
It is worth noting that the products obtained are exclusively the para-isomer, even though the ortho positions are subjected to be attacked. It seems that the bulkiness of the nucleophile prohibits that probable attack.

A strong evidence for this mechanism arises from the reaction of N-Phenylaza-15-C-5 with DMSO without using a lewis acid. In this case it is most likely that N-phenylaza-15-C-5 ring complexes with DMSO, which induces its polarization to produce the nucleophilic species as in 3, which then reacts as depicted in scheme 2.

Scheme 2

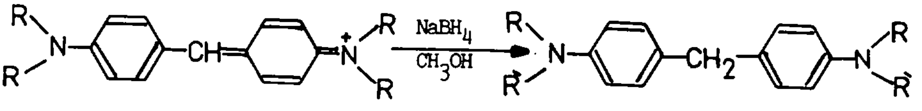


It is clear from scheme 2 that more than one conjugate anion may exist. This might be the reason behind the fact that the products were hygroscopic. Elemental analyses of the original products reveal the presence of halogen and sulfur. To increase the stability of the ionic products, they were precipitated as hexaflourophosphate salts by the addition of KPF_6.



3

Reduction with Sodium Borohydride: Further evidence for the formation of products 2(a-e) stems from the fact that these dyes can be reduced with $NaBH_4$. Thus, the crude products obtained from the reactions of N,N-dimethylaniline (2a) and N-phenylaza-15-C-5 (2e) with DMSO were reduced with $NaBH_4$ in methanol to yield exclusively compounds 4a and 4e, respectively (Eq.1).



4 (Eq.1)

Compounds 4a and 4e are fully characterized, and 4a is proved to have properties identical to those of an authentic sample. The results are included in the experimental section.

Experimental Section

Materials. Aromatic amines were of guaranteed grade and purified by distillation before use. N-phenylaza-15-C-5 (Merck, 98% pure) was recrystallized from MeOH-H_2O. DMSO purified and distilled by standard procedure. An authentic sample of compound 4a was purchased from Aldrich (98% pure).

Apparatus. All melting points were measured with Electrothermal melting point apparatus and are uncorrected. UV-Visible spectra were measured with PYE-UNICAM SP8-100 spectrophotometer. Infrared spectra were measured with a PYE-UNICAM SP3-300 spectrophotometer ^{1}H-NMR spectra were recorded on a Bruker-WP 80Y with $CDCl_3$ as the solvent; Chemical Shifts (δ) are expressed in parts per million relative to tetramethylsilane. The elemental analyses were performed at Mikroanalytisches laboratory Pascher, Bonn, West Germany.

Preparation of bis(4-N,N-dimethylaminophenyl) methenium hexafluorophosphate (2a).

A mixture of N,N-dimethylaniline (24.2g, 0.20 mol), anhydrous DMSO (30 ml) and few drops of $TiCl_4$ was heated at ca. 150°C for 1h. The solution is gradually turned blue. After cooling, water was added and the blue product was extracted with chloroform. The solvent was evaporated to yield a gummy product, which was washed with diethyl ether several times. The product was then dissolved in aqueous methanol and precipitated by the addition of aqueous KPF_6 as hexafluorophosphate salt: 27.8g (70%); IR(KBr disc) 2860, 1580, 1380 cm^{-1}; UV-Visible (methanol) 590, 3.10, 264 nm; ^{1}H-NMR 2.91 (s,12H), 6.62-7.22 (m,9H); High resolution MS, m/e 253.1712 (M^+, calcd. for $C_{17}H_{21}N_2$ 253.3663), 210.1273 (M^+-C_2H_5N, calcd. for $C_{15}H_{16}N$ 2 10.2981), 134.0970 (M^+-C_8H_9N, calcd. for $C_9H_{12}N$ 134.2005), 118.0629 (M^+-$C_9H_{13}N$, calcd. for C_8H_8N 118.1579). Analysis, calculated for $C_{17}H_{21}N_2PF_6$: C, 51.26; H, 5.28; N, 7.04. Found: C, 51.40, H, 5.35; N, 6.98.

Preparation of bis(4-N-phenylaza-15-C-5) methenium hexafluorophosphate (2e).

A mixture of N-phenylaza-15-C-5 (1.00g, 3.4 mmol), anhydrous DMSO (25 ml) and few drops of $TiCl_4$ was heated at 60°C for 45 minutes. During this time the reaction mixture turned deep blue. DMSO was evaporated under vacuum and the residual gummy product was washed several times with diethyl ether. The crude product was dissolved in chlorooform and poured on a silica gel chromatographic column, the product was eluted with 3:1 chloroform-ethanol mixture. After the solvent was evaporated the gummy product was dissolved in methanoland precipitated with KPF_6 solution to give a crystalline blue product: 1.56g (35%); IR(KBr disc, cm^{-1}) 1600, 1340, 1130; UV-Visible (Methanol, λ_{max})600, 580, 264nm; ^{1}H-NMR 3.7 (s, 40H), 6.6-7.3 (m,9H); High resolution MS, m/e 602.3570 (M^++1, calcd for $C_{33}H_{49}N_2O_8$ 602.7666), 308.1876 (calcd for $C_{17}H_{26}NO_4$ 308.3974), 295.1767 (calcd for $C_{16}H_{25}NO_4$ 295.1767). Analysis, calcd. for $C_{33}H_{49}N_2O_8PF_6$: C, 53.08; H, 6.56; N, 3.75. Found C, 52.98; H, 6.72; N, 3.78.

The same procedure was applied for the reaction of N-phenylaza-15-C-5 with DMSO without a lewis acid. However, the reaction mixture was heated at 150°C for 2.5 h. A comparable yield was obtained.

Preparation of bis(4-N-Methylaminophenyl)methenium hexafluorophosphate (2b).

A solution of N-methylaniline (10.4g, 0.10 mole) in DMSO (40 ml) was heated, in the presence of a few drops of $TiCl_4$, at 150°C for 1.5h. The solution became gradually deep pink. The solvent was removed under vacuum and the gummy residue was washed with diethyl ether several times. Then, it is dissolved in aqueous methanol and precipitated with aqueous KPF_6 as a hexafluorophosphate salt: 12.6g (68%), UV-Visible (methanol) 598, 296, 250 nm; ^{1}H-NMR 2.95 (s,6H), 6.31 (broad s,2H), 6.92-7.15 (m,9H); MS, m/e 225 (M^+, $C_{15}H_{17}N_2$), 195, 165, 119, 106. Analysis, Calcd. for $C_{15}H_{17}N_2PF_6$: C, 48.65; H, 4.59; N, 7.56. Found: C, 48.60; H, 4.72; N, 7.45.

Preparation of bis(4-N-ethylaminophenyl) methenium hexafluorophosphate (2c)

This compound was prepared as 2c. (75%), UV-Bisible (methanol) 570, 296, 244 nm; ^{1}H-NMR 2.89 (t,6H), 3.85 (q,4H), 6.29 (broad s,2H), 6.72-710 (m,9H); MS, m/e 253 (M^+, $C_{17}H_{21}N_2$), 209, 165, 133. Analysis, clacd. for $C_{17}H_{21}N_2PF_6$: C, 51.26; H, 5.28; N, 7.04, Found: C, 52.25; H, 5.33; N, 7.33.

Preparation of bis(4-aminophenyl) methenium hexafluorophosphate (2d).

The title compound was prepared as described above. (73%), UV-Visible (methanol) 542, 292 nm; ^{1}H-NMR 6.29 (broad, 4H), 6.90-7.20 (m.9H); MS 197 (M^+, $C_{13}H_{13}N_2$), 181, 165, 105, 92. Analysis, calcd. for $C_{13}H_{13}N_2PF_6$: C, 45.61; H, 3.80; N, 8.19. Found: C, 45.98; H, 3.88; N, 8.22.

Preparation of bis (4-N,N-dimethylaminophenyl) methane (4a).

Sodium borohydride (0.45 g, 12 mmol) was added to the blue solution of bis(4-N,N-dimethylaminophenyl) methenium hexafluorophosphate (4.0g, 10 mmol) in methanol. The mixture was stirred at room temperature for 1h. During this time the blue color was disappeared. Methanol was evaporated and the residue was dissovled in water and extracted with dichloromethane. The solvent was removed and the product was crystallized from methanol to give 4a as colorless crystals, 2.40 g (95%, based on the cation only); mp 88-90°C (Lit.[7] mp 89-91°C); IR (KBr disc) 3070, 1580, 1340; UV-Visible (methanol) 300, 261 nm; ^{1}H-NMR 2.88 (s, 12H), 3.80 (s,2H), 6.7-7.1 (m,8H); MS 254 (M^+, $C_{17}H_{22}N_2$), 2.10, 166, 134.

The properties are in agreement with those of an authentic sample[7,14].

Preparation of bis(N-phenylaza-15-C-5) methane (4e).

The compound was prepared as described above. IR (KBr disc) 1600, 1345, 1120; UV-Bisible (methanol) 300, 261; ^{1}H-NMR 3.60 (s, 40H), 3.78 (s,2H), 6.61-7.20 (m,8H), MS 603 (M^+ +1, $C_{33}H_{50}N_2O_8$), 295, 105.

Aknowledgment:

Support from Yarmouk University is gratefully acknowledged (project Nr. 74/84).

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