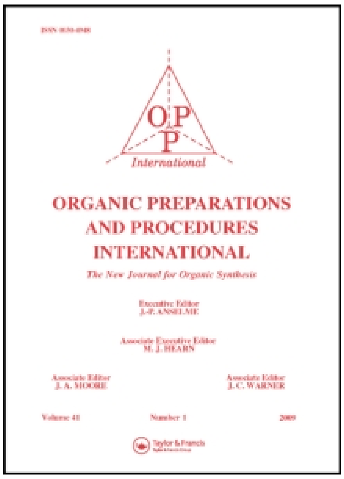

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THE SYNTHESIS OF THE DIIMINE AND THE RADICAL CATION CHLORIDE OF N,N'-DIPHENYL-*p*-PHENYLENEDIAMINE[†]

Submitted by
(03/10/88)

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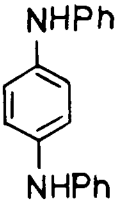
N,N'-Diphenyl-*p*-phenylenediamine (1) is a powerful antioxidant[1] which has been used in industry and in particular in the stabilization of rubber compounds. Transition metal ions, if present even in trace amounts in the rubber, have been found to decrease the efficiency of the diamine.[2] In the course of an investigation of the reaction of the diamine with metal ions,[3] we found that ferric chloride hexahydrate in acetone-water easily oxidizes the diamine to the corresponding diimine (2) or to the radical cation chloride[4] (3) which is associated in the solid state with the parent diamine (1) at room temperature. The reported procedures[1,5-7] for the preparation of the diimine 2 result in either impure products or in low yields; in addition, the reactions are conducted under vigorous conditions and the products require chromatographic separation. The radical cation chloride 3 has been isolated, in the solid state, by the reaction of the parent diamine with triphenylchloromethane;[8] in solution, the cation itself has been generated by various chemical and photochemical oxidation methods.[9]



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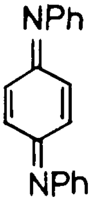

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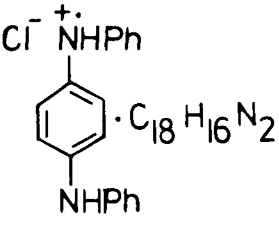

3

In the present work, the diamine 1 was reacted with ferric chloride hexahydrate using various molar and solvent ratios. When the reaction is carried out in pure acetone, the radical cation 3 is obtained in solution a a sole product. However, the diimine 2 precipitates as a second product, in addition to compound 3, when the solvent of the above reaction is changed from pure acetone to a mixture of acetone and water. The ratio of the two products 2 and 3 depends on the acetone:water ratio. As the amount of water increases, the amount of compound 2 increases. The molar ratio of the reactants seems to affect the yields but not the nature of products. Compound 2 becomes the sole product and is isolated in best yields when the water:acetone volume ratio is 4:1 and the diamine:ferric salt molar ratio is 1:3, respectively, while the corresponding volume and molar ratios for the isolation of compound 3 are 1:2.5 and 1:1, respectively (see below).

However, this reaction is being further investigated in our laboratories in an attempt to elucidate its mechanism.

EXPERIMENTAL SECTION

The IR spectra were recorded on a Pye-Unicam Sp 3-300 infrared spectrophotometer. The UV-vis spectra were recorded on a Varian DMS 100 S spectrophotometer. The ^{1}H-NMR spectra were obtained with a Bruker WP80SY spectrometer. Melting points were determined with an electrothermal melting point apparatus and were uncorrected. Microanalysis were performed by M-H-W Laboratories, Phoenix, Arizona, USA.

N,N'-Diphenyl-p-phenylenediimine (2).- A solution of N,N'-diphenyl-p-phenylenediamine (0.52 g, 2.0 mmol) in acetone (10 ml) was added dropwise to a stirred solution of $FeCl_3.6H_2O$ (1.62 g, 6.0 mmol) in water (40 ml). The reaction mixture was stirred for 3 hrs at room temperature. The precipitate was collected, washed extensively with water and minimal amount of diethyl ether. It was recrystallized from benzene and dried in vacuo at 40° to yield 0.46 g (89%) of orange crystals, mp. 188°, lit.[7] mp. 187°.

Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.68; H, 5.56; N, 10.73

The diimine 2 is insoluble in water, slightly soluble in methanol and ethanol but dissolves in acetone, dichloromethane, chloroform, nitromethane and dimethylformamide. The IR spectrum (KBr pellets) is characterized by the absence of an NH band. The following main bands are observed: 3050 (C-H); 1585, 1485, 1450 (C=C and C=N); 1220, 1180, 1125, (C-H); 860, 793, 740, 710 (C-H)cm^{-1}. The UV-vis spectrum (in acetone) exhibits two absorption bands at 445 and 327 nm, lit.[6] λ_{max}. (95% EtOH) 443, 304 nm. The shift in the frequency of the latter absorption band can be explained by differences in solvent effects; ethanol may H-bond to the diimine 2 while acetone will not. This observation supports the presence of the imine C = N-system. The ^{1}H-NMR spectrum (in CD_2Cl_2) indicates the absence of peaks in the range 3.0-6.0 ppm confirming the absence of protons on the nitrogen atoms.

The Radical Cation Chloride of N,N'-Diphenyl-p-phenylenediamine (3).- A solution of the diamine (0.52 g, 2.0 mmol) in acetone (25 ml) was added dropwise to a stirred solution of $FeCl_3.6H_2O$ (0.54 g, 2.0 mmol) in water (10 ml). The reaction mixture was stirred for 3 hrs at room temperature. The product was collected and washed with water, acetone and diethyl ether and dried in vacuo at 40° to give 0.299 (54%) of dark violet-blue solid, mp. 184° (dec.), lit.[8] mp. 183-184°.

Anal. Calcd for $C_{36}H_{32}N_4Cl$: C, 77.75; H, 5.80, N, 10.08; Cl, 6.38
Found : C, 77.62; H, 6.02; N, 10.24; Cl, 6.32

The results of the elemental analysis agree with that reported[8] for the association of the radical cation with the parent diamine in the solid state. This compound is insoluble in water, soluble in methanol and dimethylformamide and slightly soluble in ethanol, acetone, dichloromethane, chloroform and nitromethane. The IR spectrum (KBr pellets) is characterized by the presence of a series of bands in the range 3260-2800 cm^{-1}. The following main bands are observed: 1595, 1500, 1483, 1462 (C=C and N-H); 1310, 1298 (C-N); 845, 785, 738, 680 (C-H)cm^{-1}. The

UV-vis spectrum (in acetone) exhibits three absorption bands at 327, 393 and 715 nm. These values are in good agreement with those reported for the radical cation generated in solution.[9c]

REFERENCES

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1. J. Rotschova and J. Pospisil, Chem. Ind. (London), 393 (1981) and references therein.
2. I. Jitaru, M. Gutul, M. Giurginca and A. Meghea, Industria Usoara (Rom.), 28, 348 (1981); Chem. Abs., 96, 70187x (1982).
3. M. Y. Shatnawi, M. Sc. Thesis, Yarmouk University, Irbid, Jordan, July 1987.
4. The terms meri-quinoid and semi-quinone have been used in literature for the radical cation.
5. J. Piccard, Ber., 46, 1843 (1913).
6. G. Hughes and B. Saunders, J. Chem. Soc., 3814 (1956).
7. I. Bhatnagar and M. George, J. Org. Chem., 33, 2407 (1968).
8. W. Dilthey, W. Schommer and G. Escherich, Ber., 65B, 95 (1932).
9. (a) W. Dilthey and G. Escherich, ibid., 66B, 782 (1933); (b) H. Linschitz, J. Rennert and T. Korn, J. Am. Chem. Soc., 76, 5839 (1954); (c) G. Cauquis and D. Serve, Anal. Chem., 44, 2222 (1972).

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HETEROGENEOUS SYNTHESIS OF REISSERT COMPOUNDS UTILIZING POTASSIUM CYANIDE ADSORBED ON AMBERLITE XAD RESINS†

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Reagents adsorbed on solid supports have been used in a variety of organic reactions.[1] Sukata has used adsorbed potassium and sodium cyanide on Amberlite XAD resins for the synthesis of aromatic acyl cyanides,[2] cyanosilylation of aldehydes and ketones,[3] and nucleophilic substitution reactions.[4] In light of Sukata's work, we felt that the use of these potassium cyanide impregnated resins could be applied to the synthesis of Reissert compounds.[5,6]

The resins were prepared by the method of Sukata.[4] The Amberlite XAD-2, -4, and -7