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Synthesis and Characterization of Some New Dianiline Oxide Derivatives

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Abstract

Multifunctional dianiline oxide ligands from 1,3-indanedione with aniline derivatives in ethanol (abs.) then with hydrogen peroxide in gl acial acetic acid (Scheme 1) were synthesized. These dianiline oxide compounds have been characterized by C, H, N elemental analysis, FT-IR, and ^{1}H NMR spectroscopy.

Keywords: aniline oxide , indanedione, nitrone

Introduction

A big challenge facing academia and industry is the relationship of modern societies to the environment that requires reinventing the manufacture and use of materials. Synthetic methodologies now a day should be designed to use and generate substances that possess little or no toxicity to human health and the environment. Schiff bases belong to a widely used group of organic intermediates important for production of specialty chemicals, e.g. pharmaceuticals, or rubber additives (Macho et.al.,2004) and as amino protective groups in organic synthesis (Bey and Vevert, 1977, Fleet and Fleming 1969) They also have uses as liquid crystals (Adams,2000) , and in analytical(Jungreis and Thabet, 1969; Croot and Johansson, 2000; Choi et.al., 2000) medicinal (Shijun et.al., 2002) and polymer chemistry (Johnson, 2005) .

Conventionally Schiff bases have been prepared by refluxing mixtures of the amine and the carbonyl compound in an organic solvent, for example, ethanol or methanol (Sridhar et. al., 2001), but variations are known, such as treatment of the same mixture at room temperature, refluxing the mixture in heptane in the presence of acetic acid (Kunz et.al., 1991), or azeotroping the mixture with benzene in a Dean-Stark apparatus in the presence of acid (Vazzana et.al., 2004). In general, ketones react more slowly than aldehydes and higher temperatures and longer reaction times are often required as a result. In addition, the equilibrium must often be shifted, usually by removal of the water, either azeotropically by distillation or with suitable drying agents (Weingarten et.al., 1967). In recent years, environmentally benign synthetic methods have received considerable attention and some solvent-free protocols have been developed (Augusto et.al., 2006). Grinding together solid anilines and solid benzaldehydes yielded various kinds of benzylideneanilines (Schmeyers et.al., 1998). The synthesis of primary imines by condensation of 2-hydroxylaryl ketones with ammonium iodide and piperidine under solvent free conditions (Bergman et.al., 2004).

In this work we have synthesized and characterized of some new dianiline oxide compounds Derived 1,3-indanedione by oxidation diimine with peroxide in glacial acetic acid.

Expermental methods

General:

Melting points were uncorrected. NMR spectra were acquired with a Bruker Ultra Shield (^{1}H : 300 MHz) (University of AL-al-Bayt,Jordan). The chemical shifts were referenced to tetra methyl silane (TMS) as an internal standard. The elemental analysis were performed by using Euro Vector EA3000A (University of AL-al-Bayt,Jordan).

Synthesis of dianiline oxide :

General procedure:

(0.01 mole) of 1,3-indandione (1) was disolved in absolute ethanol in the presence of p-toluene sulphonic acid. Then, (0.02 mole) of aniline and its derivatives (2-6) were added and heated under reflux for (3) hrs. Then, the mixture was cooled in an ice bath for 2 hrs and yielded different colored crystal. These products treated with 5.4 ml hydrogen peroxide in 12 ml glacial acetic acid to gave dianiline oxide derivatives the residue was purified by recrystallization from benzene.

N,N'-(1H-indene-1,3(2H)-diylidene)dianiline oxide (2)

From aniline 70 % yield ; m.p. (170-172)^{o}c; CHN analysis for $C_{21}H_{16}N_2O_2$; C 76.81; H 4.91; N 8.53 Found; C 76.74; H 4.90; N 8.50. FT-IR spectra υ(cm^{-1}) 1656 cm^{-1} (C=N). δ_H(CDCl$_3$) (8.243-8.272) ppm(2H,d,a); (7.080-7.384) ppm (12H,m,b,c,d,e); 1.575 ppm (2H,s,f).

N,N'-(1H-indene-1,3(2H)-diylidene)bis(4-methylaniline oxide) (3)

From 4-methyl aniline 79 % yield ; m.p. (100-102)^{o}c; CHN analysis for $C_{23}H_{20}N_2O_2$; C 77.51; H 5.66; N 7.86 Found; C 77.47; H 5.61; N 7.85. FT-IR spectra υ(cm^{-1}) 1674 cm^{-1} (C=N). δ_H(CDCl$_3$) (8.255-8.264)ppm(2H,d,a); (7.755-7.764) ppm (2H,d,b); (7.418-7.481) ppm (8H,m,c,d); 7.282 (s, CDCl$_3$); 3.751 ppm (6H,s,e); 2.175 ppm

(2H,s,f) .

N,N'-(1H-indene-1,3(2H)-diylidene)bis(4-methoxyaniline oxide) (4)

From 4-methoxy aniline 90 % yield ; m.p. (88-90)^{o}c; CHN analysis for $C_{23}H_{20}N_2O_4$; C 71.12; H 5.19; N 7.21 Found; C 71.11; H 5.13; N 7.19. FT-IR spectra υ(cm^{-1}) 1654 cm^{-1} (C=N). δ_H(CDCl$_3$) (8.255-8.264) ppm(2H,d,a); (7.418-7.481) ppm (6H,m,b,c); 7.282 (s, CDCl$_3$); (6.629-6.669) ppm (4H,d,d); 3.751 ppm (6H,s,e); 2.175 ppm (2H,s,f).

N,N'-(1H-indene-1,3(2H)-diylidene)bis(4-bromoaniline oxide) (5)

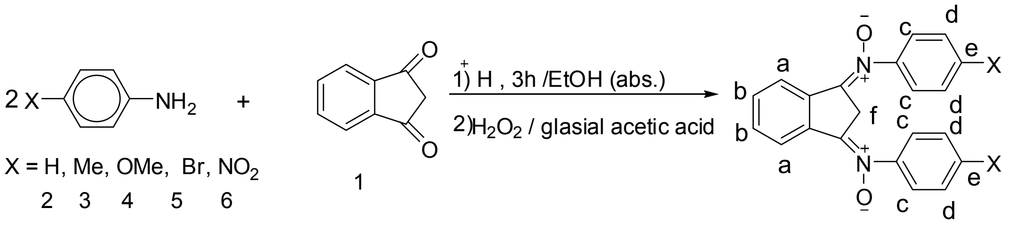
From 4-bromo aniline 68 % yield ; m.p. (202-204)^{o}c; CHN analysis for $C_{21}H_{14}N_2Br_2O_2$; C 51.88; H 2.90; N 5.76 Found; C 51.86; H 2.90; N 5.75. FT-IR spectra υ(cm^{-1}) 1637cm^{-1} (C=N). δ_H(CDCl$_3$) (8.142-8.179) ppm(4H,d,d); (7.800-7.917) ppm (8H,m,a,b,c); 7.282 (s, CDCl$_3$); 2.175 ppm (2H,s,f).

N,N'-(1H-indene-1,3(2H)-diylidene)bis(4-nitroaniline oxide) (6)

From 4-nitro aniline 65 % yield ; m.p. (250-252)^{o}c; CHN analysis for $C_{21}H_{14}N_4O_6$; C 60.29; H 3.37; N 13.39 Found; C 60.26; H 3.36; N 13.39. FT-IR spectra υ(cm^{-1}) 1670 cm^{-1} (C=N). δ_H(CDCl$_3$) (7.800-7.917) ppm(8H,m,a,b,c); 7.282 (s, CDCl$_3$); (6.629-6.669) ppm (4H,d,d); 2.175 ppm (2H,s,f).

Results and Discussion:

Treatment of 1,3-indandione (1) with aniline and its derivatives (2-6) in the presence of p-toluene sulphonic acid as catalyst in boiling ethanol gave, , then treated products with 5.4 ml hydrogen peroxide in 12 ml of glacial acetic acid stirred in ice bath for 6 hours gave, after purification by recrystallization from benzene gave dimer imino-N-oxide, derivatives in (65-90) % yield,as crystalline compounds, as shown in scheme 1. The structures of these products were established from their elemental analysis,FT-IR,C.H.N and ^{1}H NMR spectra. All the IR spectra of dimeric imine-N-oxide showed a peak at (1637-1674) cm^{-1} which appeared due to (C=N) stretching, and showed a peak at (1210-1280) cm^{-1} due to (N-O) stretching of N-oxide group. The^{1}H NMR spectra are represented in figures (1-5). All the ^{1}H NMR spectra of dimeric imine-N-oxide were characterized (Silverstien et.al., 2005; Cooper, 1980; Shriner and Hermann, 2004) by the presence of CH_3 protons of at δ=3.751 ppm, since the OCH_3 protons appeared at δ= 3.751 ppm.The elifatic protons (CH_2) to indane ring appeared at δ= (1.575-2.175) ppm. The aromatic protons rings showed doublet or multiplet signal in the region δ= (7.800-8.272) ppm due to protons at a position. The other protons at b position for this rings showed doublet or multiplet signal within the range (7.080-7.917) ppm. While protons at c position for this rings showed multiplet signals within the range (7.080-7.917) ppm. The protons at d position for this rings showed doublet or multiplet signal within the range (6.629-8.179) ppm. While the protons at e position for this rings showed multiplet signals within the range (7.080-7.384) ppm.



Scheme 1

CONCLUSION

In conclusion, a rapid, high yield, simple, practical, economic, readily available system, and convenient procedure for the synthesis of dianiline oxide derived from 1,3-indandione has been developed.

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