



## RESEARCH ARTICLE

## Total Synthesis of N,N-Dimethyl Dodecyl Amine-N-Oxide

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**Key words:****\*Corresponding Author****M.Mamatha.****Abstract**

A cheap, mild, inexpensive and environmentally friendly synthesis of N,N-Dimethyl Decocyl Amine is Reported. Oxidation of amine to amineoxide using H<sub>2</sub>O<sub>2</sub> as oxidant is done.

*Copy Right, IJAR, 2016. All rights reserved.***Introduction:-**

N,N-Dimethyl Dodecyl Amine-N-Oxide (DDAO) is a very important compound in consumer goods synthesis. It acts as a good foam stabilizer and as a surfactant in dishwash detergent. It also acts as a good antistatic agent. They are also employed as oxidants to accomplish important reactions. These long chain alkyl amine oxides are highly polar molecules and soluble in water. Due to these properties it has been extensively studied by many scientists<sup>1,2&3</sup> and has many applications in consumer goods.

Recently several methods have been developed to synthesize these amine oxides<sup>4&5</sup>. N,N-Dimethyl-N-alkyl amines are prepared by reaction of dimethylamine with an alkyl halogen compound, a fatty alcohol or an alpha olefin<sup>6,7 &8</sup>. However, these routes suffer from disadvantage of expensive raw materials and excessive waste disposal costs. There are two major routes for preparing DDAO. The former method involves the use of dimethyl sulfoxide (DMSO) in limited equivalence. The latter method involves the use of formaldehyde and formic acid. Both the synthetic routes are cost effective and high yielding.

This research paper involves the total synthesis of DDAO by a simple, inexpensive and convenient route of this stable molecule.

**Experimental:-****I Preparation of N,N-Dimethyl Dodecyl Amine (DDA)**

Two synthetic schemes have been proposed for the synthesis of DDA.

**Scheme-I:-**

Dodecylamine (20 gms, 0.108 mmol) was taken in an round bottom flask and cooled in an ice cold water. Then formic acid (5 ml, 0.162 mmol) was added drop by drop till a clear solution was obtained. To this solution was added 5.86 gms of formaldehyde. The above reaction mixture was refluxed at 80 C for 5 hrs. The crude product obtained was evaporated in a rotavacour and purified by crystallization to obtain 9.7 gms of DDA. Product formed was characterized by FTIR spectrum and <sup>1</sup>H NMR data.

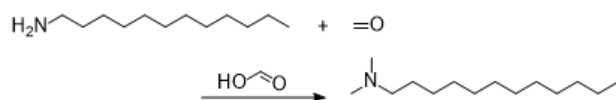


Fig.1: Synthesis of DDA by scheme I

The following mechanism has been proposed:

Dodecylamine is converted to DDA by an amine methylation process using formaldehyde and formic acid through an intermediate iminium ion. Dodecylamine (I,  $R=C_{12}H_{22}$ ) (I) reacts with formaldehyde in an acidic medium to form Schiff's base (II) which translates to N=C compound (III) by intramolecular dehydration reaction. Then oxidation-reduction reaction occurs between formic acid and N=C compound (III) to form secondary amine (IV). In a similar manner secondary amine reacts with formaldehyde and formic acid to form N,N-dimethyl dodecylamine (V).

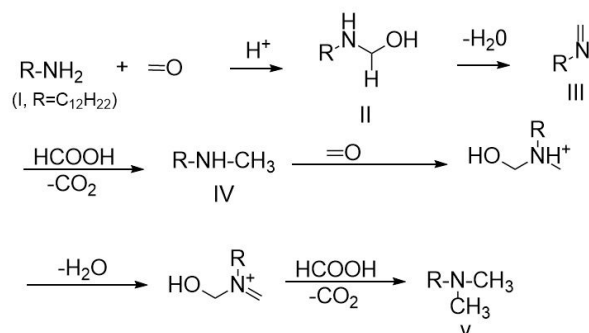


Fig. 2: Mechanism of scheme 1 synthesis of DDA

### Scheme II:-

Dodecylamine (20 gms, 0.108 mol) was dissolved in 60 mL of dichloromethane. 1.0 g of sodium sulphate was added as a catalyst. Reaction mixture was stirred at 60 C. After 10 minutes 0.2696 moles of dimethyl sulphate was added carefully and refluxed for 5 hrs. The crude product obtained was evaporated and purified by recrystallized in methanol to form pale yellow crystals of DDA.

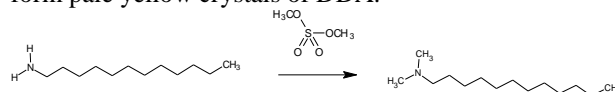


Fig. 3: Scheme 2 synthesis of DDA

### II. Preparation of DDAO:-

DDA (15 g, 0.07 mole) are taken in a round bottom flask. Then 5 g of 50% aqueous hydrogenperoxide was added slowly drop by drop over a period of 90 minutes at 70 C while stirring the solution. Then stirring is continued for another 12 hours at 70 C. To avoid gel formation, additional water can be added. To increase the yield, the reaction is left as such overnight at room temperature. Excess hydrogenperoxide in the reaction medium decomposes to water. Benzene was added to the slurry so that benzene azeotrope mixture which is formed is distilled over a rotavapour. On repeated distillation a pale yellow coloured liquid is formed. On cooling 14 gms of dense crystals of DDAO(VI) separate out.

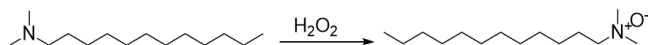


Fig. 4 : Synthesis scheme of DDAO

### Results and Discussion:-

**Materials:** Dodecylamine (99%) was purchased from Sigma Aldrich and purified by distillation under vacuum. DMSO was purchased from Aldrich (98.6%) and used as such. Formaldehyde and formic acid were purchased from Loba and used as such without any further purification.

**Methods:** A fourier transform infrared spectrophotometer (FTIR:Shimadzu 4300) was applied to record the infrared spectra of N,N-Dimethyl Dodecylamine sample by use of KBr pellets in the range of 4000-400  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded at 400 MHz on a BrukerAvance 300 spectrometer and chemical shifts are given in ppm. Samples were measured at 20 C in 5 mm NMR tubes. Chemical shifts (ppm) are referred to TMS. Melting point were recorded on anelectrothermal 9100 digital melting point apparatus IA 9100 instrument..

### Chemical Synthesis:-

In this study, both DDA and DDAO were successively synthesised and characterized by FTIR and  $^1\text{H}$  NMR spectroscopy.

### DDA:-

Yield: 78% from scheme I and 85% from scheme II, melting point -18 C. FTIR spectrum of DDA is presented in Fig. 5 and it has  $-\text{CH}_2$  stretching bands at 2924  $\text{cm}^{-1}$  ad 2854  $\text{cm}^{-1}$ . The stretching of C-N is around 1042  $\text{cm}^{-1}$ . The peak around 3435 $\text{cm}^{-1}$  may be due to asymmetric and symmetric stretching of  $\text{NH}_2$ . The peak in the range of 1410  $\text{cm}^{-1}$  and 1510  $\text{cm}^{-1}$  may be the bending mode of  $-\text{NH}_2$  and  $-\text{N}(\text{CH}_3)_2$ . It is indicated that synthetic product in DDA contains a little amount of Dodecylamine.  $^1\text{H}$  NMR(400 MHz, Fig. 6):  $\delta$  2.3 (2H,t,- $\text{NCH}_2$ -), 2.2 (6H,s,- $\text{N}(\text{CH}_3)_2$ ), 1.5(2H,- $\text{CH}_2\text{CH}_3$ ), 1.2-1.4(18H,- $\text{CH}_2$ -), 0.9 (3H,t,- $\text{CH}_3$ ).The total synthesis of DDA was indicated by a signalin the form of singlet at 2.2 ppm representing- $\text{N}(\text{CH}_3)_2$  protons.

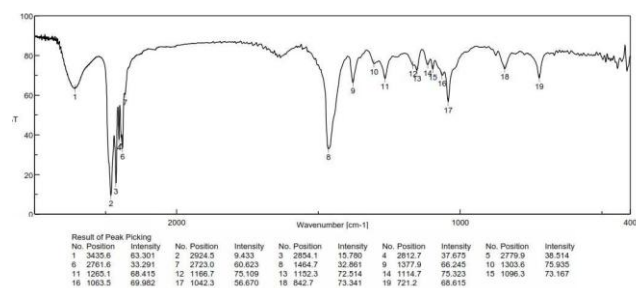


Fig 5: FTIR spectrum of DDAO

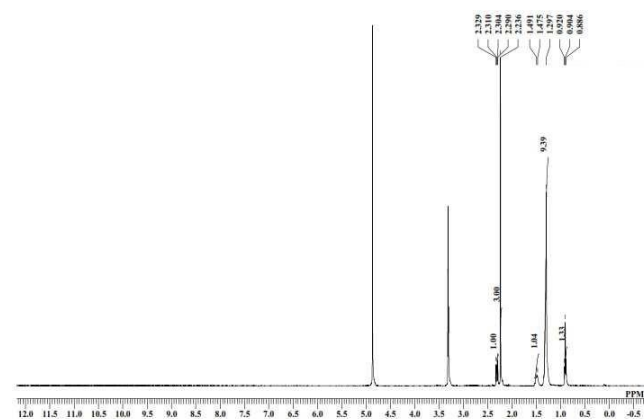


Fig 6:  $^1\text{H}$  NMR spectra of DDA

### DDAO:-

Yield: 88%, melting point 95 C,  $^1\text{H}$  NMR (400MHz, Figure 7).  $^1\text{H}$  NMR(400 MHz, Fig. 7):  $\delta$  3.25(2H,t,- $\text{NCH}_2$ -), 3.15 (6H,s,- $\text{N}(\text{CH}_3)_2$ ), 1.8-1.9 (2H,br,- $\text{CH}_2\text{CH}_3$ ), 1.2-1.3(18H,- $\text{CH}_2$ -), 0.85 (3H,t,- $\text{CH}_3$ ).A higher shift in chemical shift value of  $-\text{N}(\text{CH}_3)_2$  and  $-\text{NCH}_2$ - indicates formation of DDAO.

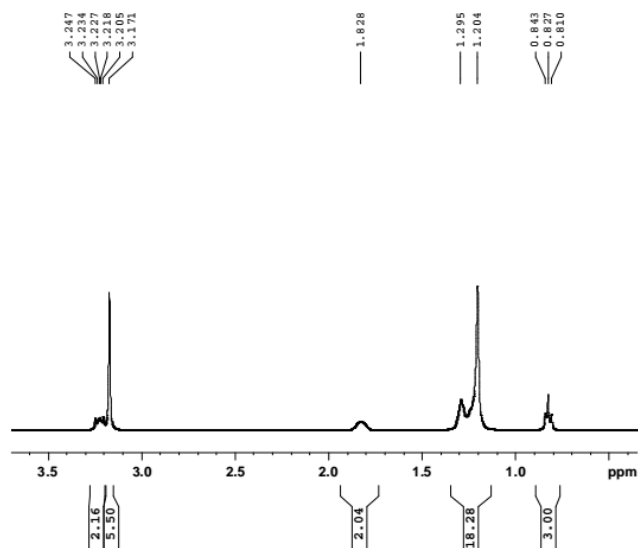


Fig. 7: <sup>1</sup>H NMR spectra of DDAO

In conclusion we have synthesized N, N-DimethylDodecylamine oxide without the use of any catalyst and by using hydrogen peroxide only.

#### Acknowledgment:-

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