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Research Article

SYNTHESIS AND STUDIES ON THE CHEMISTRY OF CYCLOHEXAMINE - N-[(2/4 - SUBSTITUTED PHENYL) METHYLENE] - N – OXIDES

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ABSTRACT

Synthesisi of cyclohexamine - N – [(P- nitrophenyl) methylene] – N – oxide with NBS. On comparing both the ^{1}H NMR and IR spctra of this brominated nitrone with unbrominated nitrone.

Keywords: *Infrared Spectroscopy, ^{1}H Nuclear Magnetic Resonance Spectroscopy, N-B Romosucinimide, Deuturated Choroform*

INTRODUCTION

Considerable development in the knowledge and understanding of nitrones is mostly due to their increasing use in cycloaddition reactions, natural product synthesis, biologically active compounds and free radical traps. The existance of dipolar character in the nitrone function has played a vital role in the development of newer synthesis approach to the formation of carbon-carbon bond (Oppolzer, 1977). Nitrones are characterized by E-Z notation rather than the Syn-anti nomenclature (Stamm, 1975). E-Z isomerisation was observed to be fast at high temerature. It was found that aldonitrones exist exclusively in the Z- form unless a ring closure is encountered that forces the existence to be in the E- form (Boyle *et al.,* 1971). Nitrones are synthesised by condensation of carbonyl compounds with N – Nanosubstitued hydroxylamines (Stamm, 1975). Alkylation of oximes at oxygen results in oxime ethers, where as nitrogen results in nitrones. Recently few methods have been reported for the synthesis of nitrones by tunstun catalyst. Oxidation of secondary amines with hydrogen peroxide has been reported to give the corresponding nitrones in a single step and in excellent yields (Muruhashi *et al.*, 1990). The other recent report being the reaction of aryl or alkyl ntrone compounds with 2 – butyl magnesium chloride to synthesis a new class of nitrones (Barohi *et al.,* 1990). Nitrones also obtained from oxaziridines and oxidation of schiff's bases.

Nitrones crystallite from anhydrous medium readily and also as adducts with various metal halides. Nitrones best dissolve in polar solvents.Very often they are hygroscopic and sufficiently basic to ferric with strong acids and adducts with Lewis acids. Alkylation at oxygen is readily achieved by heating with alkylating agents such as dimethlsulphate in an inert solvent or using a powerful alkylating agent such as triethyloxonium fluoroborate, to give corresponding o-alkylated salts (Smith, 1966). Reactions of nitrones with acylating agents such as acidchlorides, acid anhydrides, PCl_5, PCl_3, $PoCl_3$, is more complex and tends to result in rearrangement to a secondary or tertiary nitrone (Lamchen, 1968).

Experimental Methods

Melting points are uncorrected. The IR Spectra of the samples were recorded in Perkin Elmer IR 577 instrument. ^{1}H NMR Spectra were recorded in $CDCl_3$ using 90 MH_Z R-32 Perkin Elmer instrument with TMS as the internal standard. UV Spectra were recorded in PU 8800 UV/ Vis Spectraometer (Philips) using ethanol as solvent.

Synthesis of Cyclohexamine -N- [2/4 -Substituted Phenyl) Methylene] - N- oxide

(a) Benaldehyde, and 2/4 –substituted benzaldehyde were purchased from 'ALDRICH' and used as such.

(b) Preparation of Cyclohexamine Oxime

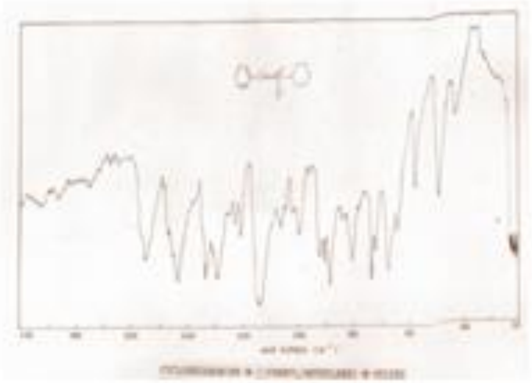
Hydroxaylamine hydrochloride (2.5 g) is added and sodium acetate (4 g) in 10 ml H_2O is taken in a small conical flask. The solution is warmed to about 40° and cyclohexane (2.5 g) is added. The vessal is stoppered securely with a cork and shaken vigorously for few minutes. The oxime separated out as a

crystalline solid. This is cooled in ice. The crystals are filtered at the pump and washed with ice water. This is then crystalised from pet.ether (60-80° c) and dried.
Yield: 2.6 g, m.p: 90°C.
(c) Preparation of N – Cyclohexylhydroxylamine from cyclohexaonone oxime using sodium cyanoborohydride/ acetic acid.
To the stirring acetic acid (75 ml) at 25° C under nitrogen atmosphere are added cyclohexamine oxime (3.48 g, 30.9 mmole) and sodium cyanoborohydride (2.79 g, 45 mmole). The mixture is stirred for 3 h_r and then water is added. The mixture is made basic with sodium hydroxide (pellets) and the resulting white solid is collected. The aqueous filterate is extracted with ether and the ether extracr is dried and concentrated in vacuo to affored a white solid. The combined solids are recrystallised from ether to give N – Cyclohexylhydroxylamine as colorless flakes. Yield: 2.88 g (81%), m.p: 138 - 139° c.

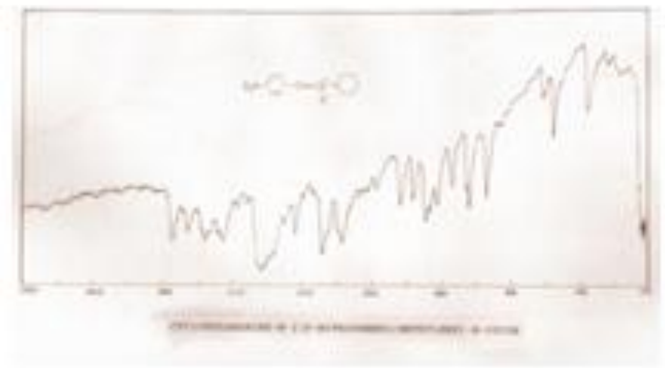
RESUTS AND DICUSSION

IR Spectra data

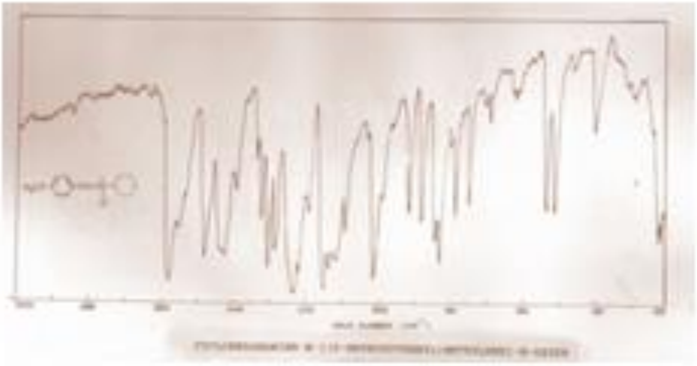
Frequency in cm^{-1} for	Cyclohexamine-N-[(Phenyl) Methylene]-N-oxide	Cyclohexamine-N-[(p-nitrophenyl)Methylene]-N- oxide	Cyclohexamine-N-[(p-methoxy phenyl)Methylene]-N-oxide
C=N	1545	1555	1580
N-O	1130	1140	1150



Cyclohexamine-N-[(Phenyl) Methylene]-N-oxide



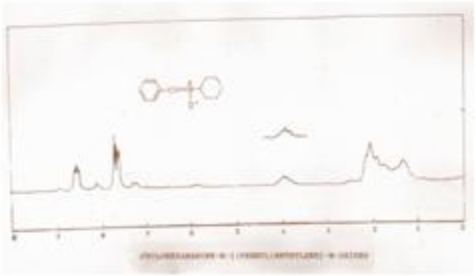
Cyclohexamine-N-[(p- nitrophenyl) Methylene]-N-oxide



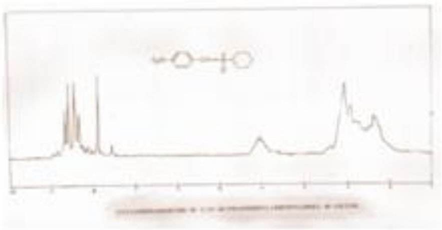
Cyclohexamine-N-[(p-methoxy phenyl) Methylene]-N-oxide

^{1}H NMR data

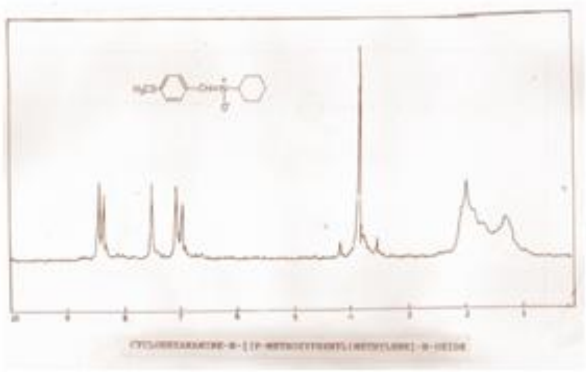
Postions	**Cyclohexamine-N-[(Phenyl) Methylene]-N-oxide**	**Cyclohexamine-N-[(p-nitrophenyl)Methylene]-N- oxide**	**Cyclohexamine-N-[(p-methoxy phenyl)Methylene] -N-oxide**
Alicylic methylene hydrogen	1.0-2.20, 10H, m	1.1-2.2, 10H, m	1.1-2.2, 10H, m
C=N	3.95,1H, m	4.10,1H, s	3.80,1H, m
α-H	7.70,1H,s	7.90,1H,s	7.50,1H,s
C_2 and C_6-H of aryl ring	8.55,2H,d	8.65,2H,d	8.40,2H,d
C_3, C_4 and C_5-H of aryl ring	7.65,3H,m	8.40,2H,d	7.00,2H,d
OCH_3	-	-	3.85,1H,s



Cyclohexamine-N-[(Phenyl) Methylene]-N-oxide



Cyclohexamine-N-[(p- nitrophenyl)Methylene]-N- oxide



Cyclohexamine-N-[(p-methoxy phenyl)Methylene]-N-oxide

Synthesis of Cyclohexamine -N- [(Phenyl) Methylene] - N- oxide

Cyclohexylhydroxylamine (1.3 g, 0.01 mole) obtained as above, benzaldehyde (1,28 g, 0.01 mole) and benzene (60 ml) are taken in a 250 ml R.B. flask. The mixture is heated for 1.5 h_r on a steam bath and the resulting water is removed azotropically. Evaporation of the remaining solvent and cooling of the residual oil resulted in Cyclohexamine -N- [(Phenyl) Methylene] - N- oxide as red prisms. This is recrystallised from pet.ether (40-60° C).Yield: 2 g (80.6 %), m.p: 81 - 83°C.

Synthesis of Cyclohexamine -N- [(p- nitrophenyl) Methylene] - N- oxide

Cyclohexylhydroxylamine (1.560 g, 0.01 mole), p-nitrobenzaldehyde (1.51 g , 0.01 mole) and alcohol (60 ml) are taken in a 250 ml R.B flask. The mixture is refluxed for 1.5 h_r on a steam bath. The solvent is then evaporated. On cooling Cyclohexamine -N- [(p- nitrophenyl) Methylene] - N- oxide crystals are formed. It is recrystallised from pet.ether (40-60° C).

Yield: 1.9 g (76 %), m.p: 89 - 91°C.

Synthesis of Cyclohexamine -N- [(p- methoxy phenyl) Methylene] - N- oxide

Cyclohexylhydroxylamine (1.560 g, 0.01 mole), p-methoxybenzaldehyde (1.56g, 0.01 mole) and alcohol (60 ml) are taken in a 250 ml R.B flask. The mixture is refluxed for 1.5 h_r on a steam bath. The solvent is then evaporated. On cooling Cyclohexamine -N- [(p- nitrophenyl) Methylene] - N- oxide crystals are formed . It is recrystallised from pet.ether (40-60° C). Yield: 2.4 g (91 %), m.p: 92 - 94°C.

Conclusion

(i) These compounds show IR absorption 1540 ± 20cm^{-1} (due to C=N str.) and 1135 ± 15 cm^{-1} (due to N-O str.) that are characteristic of nitrone function. This together with the absence of carbonyl frequency around 1751 cm^{-1} confirms the formation of nitrones.

(ii) The ^{1}H NMR spectra of all these compounds were characterised by their azomthine absorption signal 7.70 to 8.05 ppm apart from other signals due to the aromatic protons and other protons present in them. It can be noticed that when there is an electron withdrawing substitution in the para position of the α – aryl ring, the azomethane is shifted to downfield region by approximately 0.2 ppm. In the case of electron releasing substitution at the para position, the same hydrogen is shifted to the upfield region by 0.2 ppm.

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