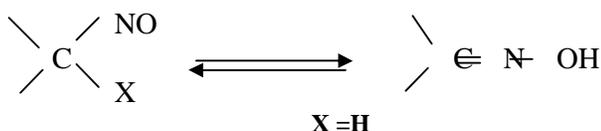


The tautomeric rearrangement to oximes, which is dominant reaction of primary and secondary nitrosoalkanes, appears to be irreversible. It can occur on molten or in solution, and may proceed more rapidly than dimerization. The vapour phase isomerization of nitroso alkanes appears to involve intermolecular hydrogen transfer. Polar solvent, strong acid and bases, and

nitric oxide accelerate the isomerization, and for basic catalysis proton removal α to the proton group is presumably important. The rate of rearrangement of secondary bis nitroso compound catalyzed by sodium hydroxide is independent of concentration of base, suggesting that the rate-limiting stage is dissociated to the monomer [6,7].



Scheme (2)

Various methods [8,9] have been reported regarding the synthesis of aliphatic and aromatic C-nitron (N-Oxide) compounds. Most of these compounds are obtained by oxidation of corresponding amine or imine, by pyrolysis of the corresponding aryl nitrite or by the action of the nitric oxide and chlorine hydrocarbons in ultraviolet light. This work describes the action of sulphuric acid (H₂SO₄) with nitro oxime which has the advantage of making the oxidation of the nitron compounds easy and in one step, in good yield and with retention of the α -carbon system. The oxidation is produced at least 94% nitron dimer, although recrystallisation reduced the yield to 70% when reaction is carried out on a small scale.

The aliphatic and aromatic nitrones are rapidly dimerize and only in case of these were any of tautomeric oxime isolated [10]. The stability of these compounds have been commented on previously, and is, of course, the reason why oximes are not formed to any major extent in this reaction. The stability of some of the dimers was quite remarkable. The generally favored preparative method of dinorborna-5-ene pyrazine N,N-dioxide involving the condensation of 2-nitro oxime norborna-5-ene by sulphuric acid as a catalyst, this reaction based on converting the dimer nitrosite to monomer nitro oxime by reduction using alcoholic base (5% sodium hydroxide). Resulting pale white crystalline material 70% (R_f = 0.44)

Experimental:

1- Spectroscopic measurements

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer; 400.13MHz for proton and 100.13 MHz for carbon, in CDCl₃ using TMS as internal standard, at University of Exeter (UK); infrared spectra were

recorded on a Shimadzu FT-IR model 8400 (KBr disk); Ultraviolet spectra were recorded on a Spectro Scan 80D UV-Visible Spectrophotometer; CHN analysis was carried out on Shimadzu 8011 (Syria).

2- Preparation of Di-Norborna-5-ene Pyrazine N,N-dioxide

i) Preparation of Trans Norborna-5-ene Nitrosite Dimer (TNND)

Trans norborna-5-ene nitrosite dimer was prepared from reaction 2,5-norbornadiene with dinitrogen trioxide

(N₂O₃) as described elsewhere [11] and was characterized by melting point, CHN, UV, IR and NMR spectra.

ii) Preparation of 2-Nitro Oxime Norborna-5-ene Compound:-

Dissolve TNND 2.4gm (0.01mole) in 40 ml acetone and add to 50ml of 5% alcoholic sodium hydroxide, the mixture was stirred, (the temperature was to 55⁰C) .After 3hr the solution was filtered and

treated with acetic acid to give the crystalline acetic acid salt, which could be readily regenerated to the free 2-nitro oxime norborna-5-ene pale yellow crystals m.p. (94-96⁰C).

iii) Preparation of Di-Norborna-5-ene Pyrazine N, N-Dioxide:-

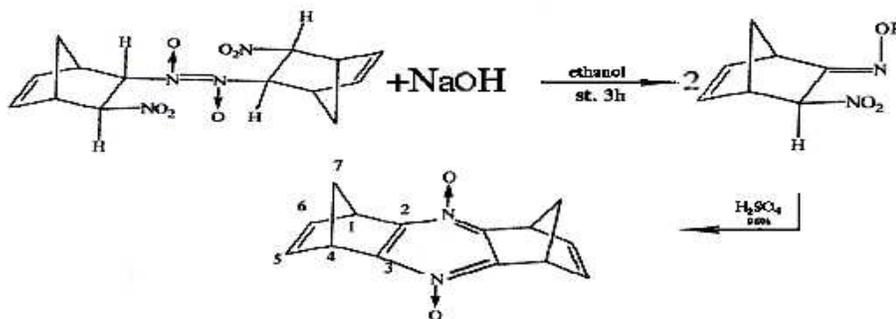
A finally crystals sample of 2.4gm (0.01mole) 2-nitro oxime norborna-5-ene was introduced in small portions at a time to 10ml of concentrated sulphuric acid (96%) at ⁰C with mechanical stirring, the slurry was gradually warmed to ambient temperature and allowed to stir for 36hr, made basic with 2N NaOH solution and extracted several times with ethyl acetate and washed with light petroleum afforded yellow oil compound. Crystalization using chloroform gave white crystals m.p. (132-

134⁰C). CHN analyzer Calc. for C₁₄H₁₂N₂O₂ (%); C,70.000 H, 5.000 N, 11.667 found C, 69.553 H, 5.287 N, 11.421 ; Ultraviolet absorption in CH₃Cl λ_{max} 298 and 246nm ; Infrared absorption 3067 (CH) ,1629(C=C) , 1589 (C=N) ,1307(N-O) , 1150(C-N). ¹HNMR in CDCl₃ δ_H (ppm) 1.9s (4H), 4.3m (2H). ¹³CNMR in CDCl₃ δ_C (ppm) 27.76 C₁, 144.00 C₂ , 132.22 C₃ , 38.77 C₄ , 126.02 C₅ , 128.02 C₆ , 32.27 C₇.

Result and Discussion:

The intermolecular application of nitro-oxime or hydroxylamine-oxime condensation using readily available N,N-dioxides provides general synthetic routs to

six membered cyclic Schiff base N-oxide .Cyclization of this type of the reaction is shown in scheme (3).



Scheme (3)

The method of the preparation of oxime from nitrosite dimer has been known for many years ago [12]; it was developed after obtaining poor yields with sodium hydroxide. Decomposition of the dimer nitrosite in the presence of alcoholic sodium hydroxide was fast and gave blue compound (monomer) in solution, no stable, and conversion rapidly to the nitro oxime and gives oil, recrystallisation in ethanol to give pale yellow crystal in good yield (85%). The acid catalyzed condensation occurs when nitro oxime converts to hydroxylamine oxime and has been treated with concentrated sulfuric acid. This reaction may involve the elimination of hydroxylamine as intermediate along with accompanying oxidation; the major product is the pyrazine *N,N*-dioxide. Elimination [13] of hydroxylamine oxime, which can be performed or prepared by a suitable condensation reaction, provides the crucial step in a number of synthetic methods leading to nitrones. The nitrone compound was concluded to be nitrone dimer from evidence of their relative stability to heat and alkali, from their UV, IR and NMR data. This nitrone compound required heating up 10-20 °C above their melting point before the change from colorless liquids (melt dimer) to deep oily monomer [14], further heating caused isomerisation to the oxime usually as a mixture of syn and anti of the isomers. A 10% solution of nitrone dimer in chloroform gave only a very yellow color when heated to 100°C in sealed tube; presumably, insufficient monomer was present at any one time to

give the pronounced oil color indicative of gross dissociation to the dimer. All the nitrone dimers studied were fairly stable in organic solution at room temperature (25°C) for several hours, but they isomerised to oxime on prolonged warming [15, 16]. The electronic spectrum (UV) was recorded at 25°C exhibits two bands, Fig (1), the first transition band 246nm (π - π^*) is attributed to the double bond of the compound while the other transition 298nm (π - π^*) is attributed *N*-oxide group.

The characteristic bands in the infrared (IR) spectrum in Fig (2) of the compound at 1629, 1307, and 1150 cm^{-1} indicate the presence of (C=N), (N-O) and (C-N), this fact and the elemental composition suggests the presence of one (N-O) group for each C_7 unit in the dimeric C_{14} species. The ^1H NMR spectrum Fig (3) exhibits three resonance absorption signals 1.9, 4.3 and 6.7 ppm, the first signal due to the proton of $\text{C}_1, \text{C}_4, \text{C}_7$. The second region of resonance signals is due to the proton of C_5, C_6 . The other signals caused by CDCl_3 solvent.

The ^{13}C NMR spectroscopy has given interesting structural information for *N*-oxide compounds, the spectra of pyrazine *N,N*-dioxide, Fig (4), seven signals are shown. Three are caused by carbon atoms of $\text{C}_1, \text{C}_4, \text{C}_7$ in addition to two signals for C_5, C_6 , and two lines for C_2, C_3 (cyclic pyrazine) [17]. The other signals are signals for CDCl_3 solvent (72ppm).

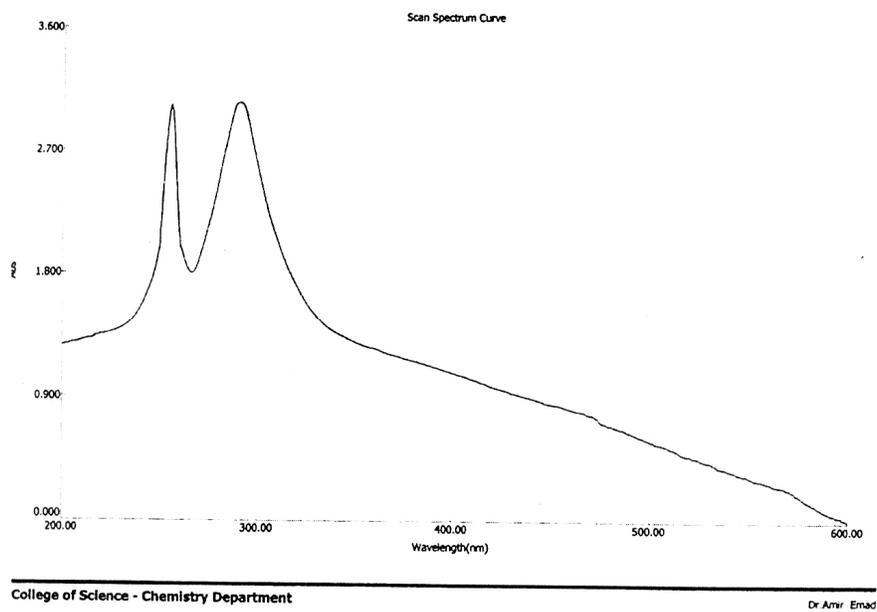


Fig (1) UV Spectra of Di-Norborna-5-ene Pyrazine N,N-Dioxide

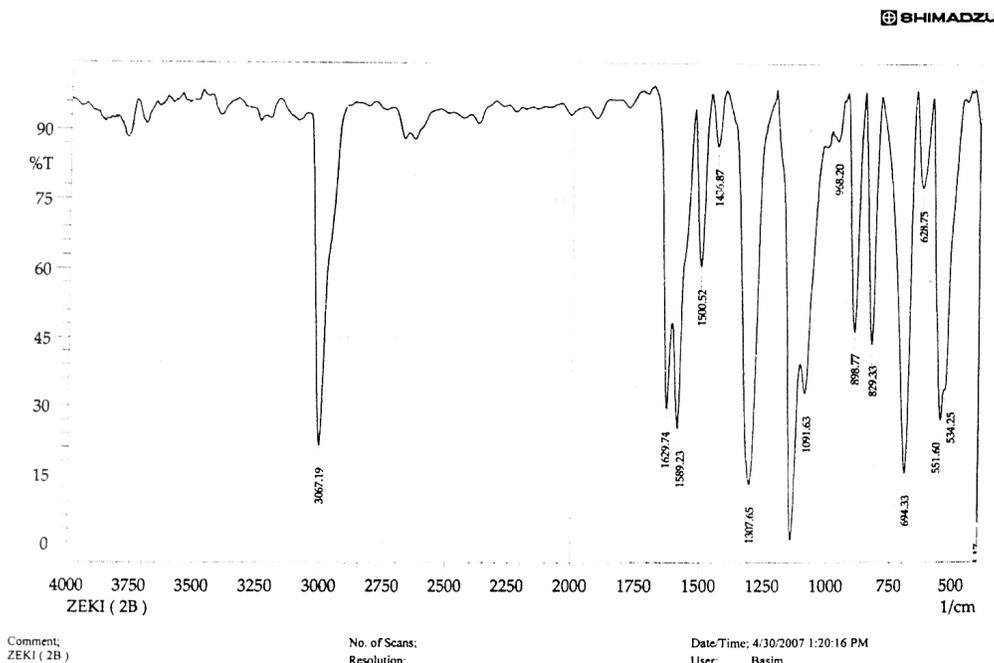


Fig (2) IR Spectra of Di-Norborna-5-ene Pyrazine N,N-Dioxide

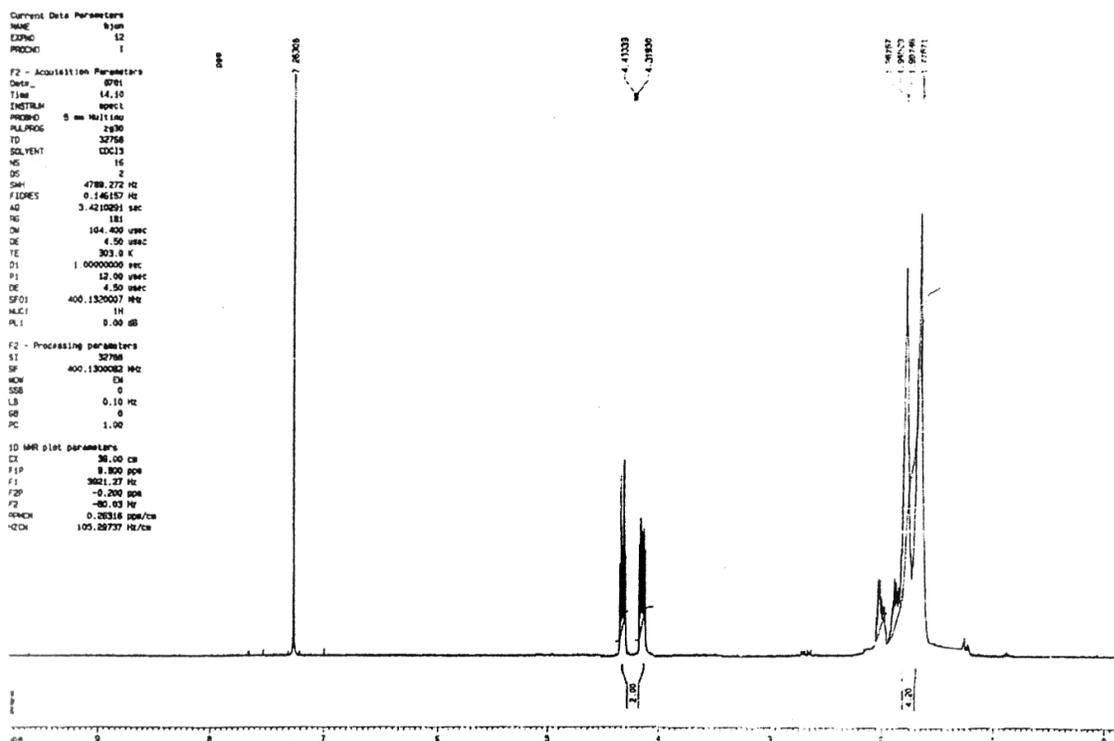


Fig (3) ¹H NMR Spectra of Di-Norborna-5-ene Pyrazine N,N-Dioxide

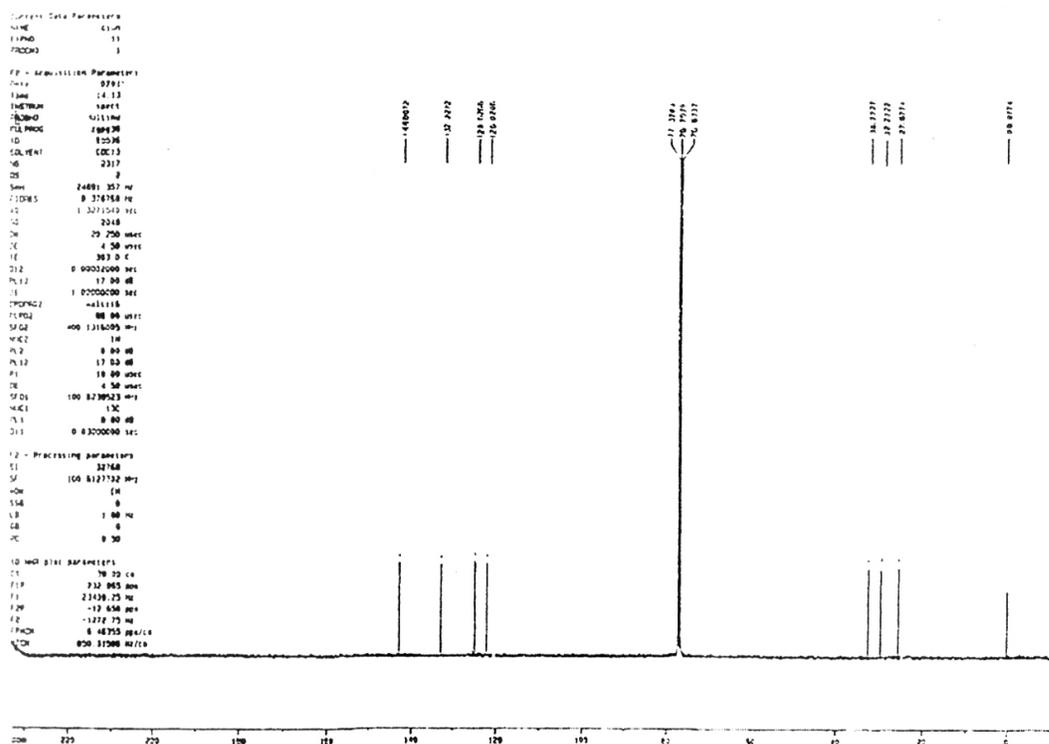


Fig (4) ¹³C NMR Spectra of Di-Norborna-5-ene Pyrazine N,N-Dioxide

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تحضير وتشخيص صفات المركب داي نوربورنا-5-ين بيرازين

ن، ن- داي اوكسايد

زكي عصمان ناصر الشمخاني

قسم الكيمياء- كلية العلوم- جامعة البصرة

المستخلص:

حضر مركب داي نوربورنا-5-ين بيرازين ن، ن- داي اوكسايد من خلال خطوات تفاعل ترانس دايمر نوربورنا-5-ين نايتروزيت مع هيدروكسيد الصوديوم الكحولي لتكوين النيترو اوكزايم وأخيرا تكوين دايمر النيترون بوساطة التكتيف مع حامض الكبريتيك المركز بنسبة 96% . وتم تشخيص المركب الأخير باستخدام تحليل العناصر الدقيق ومطيافية الفوق البنفسجية وتحت الحمراء والرنين النووي المغناطيسي للهيروجين والكاربون 13 .