Synthesis of Di -Acyl Triazene – N – Oxide

M. O. Edema*. and S. I. Onyeka
Chemistry Department, University of Benin, Benin City Nigeria.
E- mail:oliremay@yahoo.com

ABSTRACT

Diacyl triazene – N – oxides were synthesized by reaction of p- nitroso, N,N-dimethyl aniline with some acyl hydrazines. The product yield varied from 56% - 80.8%. The conditions for optimum yields and spectral characteristics of the products are reported.

INTRODUCTION

Triazene – N- oxides reported so far are mainly of the type $R^1 – N = NH – NHR^{11}$ where R^1 and R^{11} are alkyl or aryl groups[1,2]. Hoesch and Koppel[3] however reported the synthesis of unsymmetrical disubstituted triazene – N – oxide from N-aminophthalimide and nitrosobenzene via the formation of the phthalimidonitrene. Triazenes – N – oxides have been shown to form brightly coloured metal complexes and may therefore be used as complexing agents in metal ion analysis[4]. Some have also been reported to show anti-inflammatory activity[5].

This work is aimed at preparing diacyl triazene – N – oxides from p- nitroso-N,N-dimethylaniline with benzoyl hydrazine and six other substituted benzoyl hydrazines. The conditions for optimum yield were also determined.

EXPERIMENTALS

The p-nitroso-N,N-dimethylaniline (p-NDA) was prepared by the reaction of N,N-dimethyl aniline and nitrous acid [6] while the acyl hydrazines were prepared by the method reported by Chaco and Liver[7] . The acyl hydrazines prepared were:

1 Benzoyl hydrazine

2 o-methylbenzoyl hydrazine
3 m-methylbenzoyl hydrazine

4 p-chlorobenzoyl hydrazine
5 o-chlorobenzoyl hydrazine

6 p-aminobenzoyl hydrazine
7 isonocotinic acid hydrazide

Preparation of the Triazene – N – oxide

Two methods were used for the synthesis.

Method 1 Direct Reaction

0.015mol of the p-NDA was mixed with $2cm^3$ of concentrated HCl and dissolved in $80cm^3$ of distilled water. 0.01mol of the acyl hydrazine was dissolved in minimal distilled water and both solutions were kept in a preheated water bath at 30 - 50°C to equilibrate. Both solutions were then mixed and the pH adjusted with sodium ethanoate to between 2 and 5 and left for 6hours. The product was filtered, washed with cold distilled water, air-dried and weighed. The precipitate formed was purified by dissolving in tetrahydrofuran, filtered and re-precipitated with petroleum ether.

---

* *Author for correspondence*

Method II Reaction via Nitrene

Lead tetraacetate was prepared by methods described by Vogel[6]. 0.01mol of the lead tetraacetate was dissolved in acetic acid and 0.10 mol of the acyl hydrazine was put into the acetic acid mixture, stirred and then poured into 130cm^3 of water. 0.15 mol of the p-NDA was mixed with 3.5cm^3 of acetic acid and dissolved in distilled water. Both solutions were regulated to varing pH of 4 – 5 using sodium ethanoate and mixed. The mixture was kept in a regulated water bath for 6hours and then the product was filtered out, air dried and weighed.

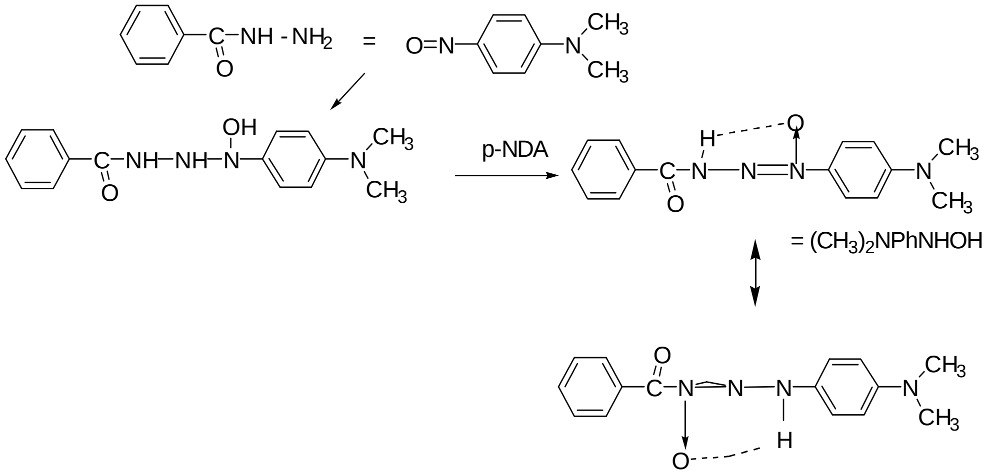
The product was washed with cold distilled water and air-dried, then purified by dissolving in tetrahydrofuran, filtered and re-precipitated with petroleum ether.

The melting point, UV and IR spectrum of the purified products were determined.

RESULTS AND DISCUSSION

The reaction scheme is

Method I



Method II

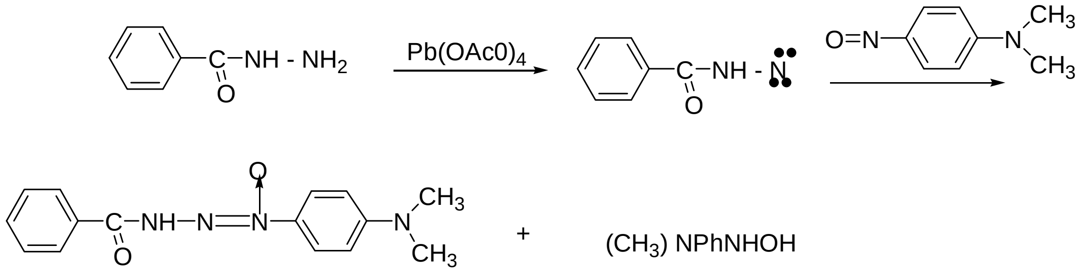


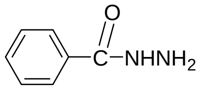
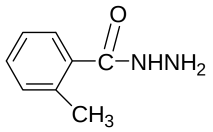
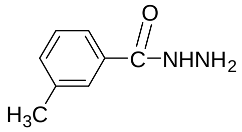
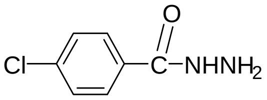
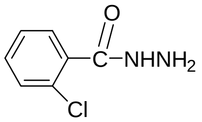
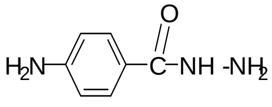
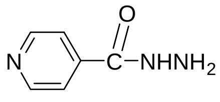
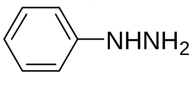
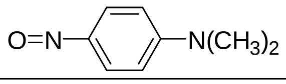
Table 1 shows the physical and spectral characteristics of the products.

The conditions for optimum yield for method I were pH 4-5, temperature 50°C; mole ratio 3:2 p-NDA : acyl hydrazine. For method II it was pH 5, temperature 40°C; mole ratio 3:2 p-NDA: acyl hydrazine. The products from methods I and II had the same melting point and spectral characteristics.

The triazene – N – oxides were found to be soluble in aqueous alkaline medium but insoluble in acidic medium. This may be due to abstraction of the N – oxygen by the base to form H_2O.

The para and meta substituted isomer were found to have higher yield than the ortho substituted isomers probably due to steric effect.

Table 1: Physical and spectral characteristics of products

S.N	Hydrazine	Colour / M.pt	UV λ_{max} (E_{max}) (nm)	IR cm^{-1}	Yield %
1	Benzoyl 	Black solid 186 - 187	480 (2673) 400 (5180) 353 (11195) 280 (6627)	3280 1600 1530 1265	80.8
2	o- methyl benzoyl 	Black solid 198 - 199	480 (4470) 400 (8609) 392 (7285) 353 (7847) 265 (13411)	3420 1650 1600 1570 1250	58
3	m- methyl benzoyl 	Black solid 189 - 190	476 (1862) 340 (29795) 300 (10428) 270 (12291) 220 (3728)	3250 1660 1600 1280 1250	88.7
4	p- chloro benzoyl 	Yellowish brown solid 212 - 213	480 (6369) 385 (7166) 300 (5308) 270 (6900) 250 (6369) 225 (5838)	3220 1660 1590 1520 1270	70.0
5	o- chloro benzoyl 	Brown 190 - 191	480 (16631) 390 (20170) 300 (17693) 270 (20878)	3410 1650 1560 1250	57.5
6	p-amino benzoyl 	Black 224 - 225	434 (13155) 390 (8970) 300 (12159) 270 (13554)	3360 1690 1590 1520 1285	82.13
7	Isonicotinic acid hydrazide 	Black 188 - 189	473 (18523) 430 (22916) 400 (22441) 352 (26716) 270 (35740) 235 (36690)	3320 1665 1600 1520 1270	36.5
8	Phenyl hydrazine 	Yellow liquid	423 (29,000) 273(5750)	3430 3240 1600 1510,1240	
9	Para- nitroso, N,N- dimethyl aniline 	Green solid 84 - 85	425 (34,340) 275 (22,827) 225 (43,307)		

The strong IR bands in the region 1650 – 1695cm^{-1} indicate a conjugated carbonyl system. Bands between 3220 – 3430 cm^{-1} indicate H – bonded N – H group while the bands at 1240 – 1290 cm^{-1} indicate the azoxy group –N = N-[8].

UV λ_{max} at 370nm seems characteristics of triazene – N – oxide when the acyl group is attached to N-1 or N-3. The UV spectrum of the triazene – N – Oxide of phenyl hydrazine (1, 3-diaryl) is similar to that of p-NDA (table 1, nos 7 & 8);with a slight bathochromic shift of the λ_{max} (423nm to 425nm, 273nm to 275nm) with accompanying marked increase in E_{max}. In the triazene –N-oxide from benzoyl, o- and m-methyl benzoyl, o- and p-chlorobenzoyl, the λ_{max} at 423nm was absent rather, there was a band between 476nm to 480nm.

Mass spectra of the 3- benzoyl – 1- (4'-N,N-dimethylaminophenyl) triazene – N-oxide gave peaks supportive of the structure:

284 - M^+ (very small)

164 - Due to breakage at bond α to the azo bond. ($C_6H_5CON = N- N= OH^+$)

150 - $(CH_3)_2N – C_6H_4$ - NO

120 - Due to breakage at bond α to the azo bond $(CH_3)_2N – C_6H_4$

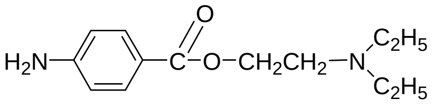
105 - base peak $C_6H_5C=O$ characteristic of carbonyl systems.

Degradation of the 3 - benzoyl – 1- (4'-N,N-dimethylaminophenyl) triazene – N-oxide gave pure benzoic acid also confirming the presence of the benzoyl function.

CONCLUSION

This work has shown that 3-acyl triazene - N – oxide can be prepared by the Fisher and Wacker method (method 1) and by the Hoesch and Koppel method (method 1). The spectral analysis supports the assigned structure for the triazene – oxide.

It would be interesting to investigate the pharmacological properties of these triazene – N – oxides as Novocain, a derivative of p-aminobenzoic acid, is used in anesthetics.



The replacement of the –O-$CH_2CH_2N(CH_3)_2$ by the triazene unit may give different pharmacological activity to the compound.

ACKNOWLEDGEMENTS

I wish to thank Dr Tempesta of Analytical Service Centre Atlanta, USA for providing the mass spectrum and the University of Benin for providing the research grant for this work.

REFERENCES

1 Smith, R.H., Denlinger, C.L., Kupper, S.R. and Michejda, C.J.; J. Am. Chem. Soc. 106 (1984) 1056 – 1059.

2 Fisher, O. and Wacker,; L. Chem. Ber 22 (1889) 622.

3 Hoesch, L. and Koppel, B.; Helv. Chem Acta 64:3 (1981) 868.

4 Chatlangya, P.D., Bhander, C.S. and Songani, N.C.; J. Indian Chem. Soc. 54:10 (1977) 1001.

5 Miesel, J.L., (Lily H. Co editors); US Pub. Pat. Appl. B. (1976) 10 February.

6 Vogel, A.I.; A textbook of Practical Organic Chemistry 4th Edn. p 345, 677 Longman Group Ltd, London 1976.

7 Chaco, M.C. and Lyer, B.H.; J. Org. Chem. 25(1960) 186.

8 Nakanishi, K.; IR Absorption Spectroscopy. p 51 Holden day, San Francisco and Nankado Company Tokyo 1962.

Received: 12/5/06
Accepted: 12/5/06