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Comparing of 5-Nonylsalicylaldoxime and Salicylaldehyde Characterization Using Magnesium Salt Formylation Process

Zeinab Pouramini and Ali Moradi*

*Department of Chemical Engineering, College of Engineering, Shahid Bahonar Univesrty of Kerman, P.O Box 76175-133, Kerman, Iran. *E-mail: moradi@mail.uk.ac.ir, alimoradi2006@yahoo.com*

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ABSTRACT. 5-Nonylsalicylaldoxime and salicylaldehyde are two derivatives of phenolic compounds which are very applicable materials in industries. Formerly the formylation of phenolic derivatives were carried out by Rimer-Tiemann method. In this work both of these two materials were synthesized by magnesium meditated formylation technique and their structural characterizations were compared by instrumental analysis technique. In order to achieve a selectively orthoformylated product, the hydroxyl group of nonylphenol (or phenol) was first modified by magnesium methoxide. The nonylphenol magnesium salt was then formylated by paraformaldehyde. The oximation reaction was finally applied to the prepared nonylsalicylaldehyde magnesium salt by liquid extracting via water and acid washing and other extractions. The solvent was finally removed by evaporation under reduced pressure. Some instrumental analysis such as ^{1}H-NMR, GC/MS and FT-IR spectra were taken on the product in order to interpret the reaction characterization quantitatively and qualitatively. The formaldehyde and oxime functional groups of two compounds were investigated through ^{1}H-NMR and FT-IR spectra and were compared. The yield of methoxilation was very good and the yields of formylation and oximation reactions were about 90%and 85% respectively. The orthoselectivity of formylation reaction were evaluated by comparing of the relevant spectra. The GC/MS spectra also confirmed the obtained results.

Key words: Nonylsalicylaldoxime, Salicylaldehyde, Formylation, Characterization

INTRODUCTION

Early works on the solvent extraction of metals show that alkylsalicylaldoxime bearing branched alkyl chains could be used as an effective extractants in the separation and hydrometallurgical recovery of valuable metals especially copper.[1-3] The outstanding characteristics of alkylsalicylaldoxime are mainly its high extractive strength and the rapid copper transfer from aqueous phases to organic phase.[4] Demand for its production is being increased highly by the development of the new copper extractions process such as microbial extraction and pressure leaching too.[5,6] Therefore, the necessity of having some new investigation on the production of alkylsalicylaldoxime particularly nonylsalicylaldoxime and improving its extraction abilities is inevitable. Moreover the method of hydroxybenzaldehyde or salicylaldehyde production is similar to salicylaldoxime. It has many applications in chemical industries. The main application of salicylaldehyde is in the manufacture of coumarin. Coumarin is an important commercial chemical used in soaps, flavors and fragrances and electroplating. Furthermore, salicylaldehyde is the forerunner of aspirin.[6,7]

2-Hydroxylbenzaldehyde has so far been synthesized according to the well-known Reimer-Tiemann reaction in which phenol is reacted with chloroform in the presence of a powerful basis such as potassium hydroxide. This process besides of having the difficulty of handling with chloroform has some significant problems such as low yield of reaction, fair orthoselectivity and the necessity of a large amount of chloroform consumption.[5-8]

In order to reduce the difficulties of the mentioned method of formylation, various new techniques have been presented up to now and the formylation of alkyl phenol derivatives are argued and promoted frequently.

In 1994, Aldred et al.[9] discussed the deprotonation of phenols using magnesium methoxide. Many other articles have investigated the preparation of phenolic aldehydes and its derivatives using the protonation of phenol.[4,8-14]

A modified duff reaction, as described by Lindoy et al.[15] is a much simpler procedure than Levin method but its main disadvantage is the lack of regioselectivity in the formylation process, substitution was occurred in both the ortho and para positions to the phenol and diformylated products were common.[4]

Casiraghi et al.[16] reported that the reaction of paraformaldehyde and magnesium phenoxide, produced from phenol and ethylmagnesium bromide in benzene as solvent in

the presence of stoichiometric mount of hexamethyl phosphoric triamide (HMPTA) resulted in formylation exclusively at the ortho position.[17] An improved method by Skatteboll in the absence of HMPTA has been reported too.[18] The ortho-formylation was carried out by paraformaldehyde and magnesium bis (phenoxide) successfully. Magnesium phenoxide was prepared from the reaction of phenols and magnesium methoxide in methanol as the cosolvent instead of HMPTA.[9]

Therefore, once the mono-formylation is selectively desired and more than one site for incorporation of the -HC=O group is possible, the Levin method usually is chosen, which involve magnesium mediated ortho-formylation.

Oximation of salicylaldehyde to salicylaldoxime due to the strike hindrance of hydroxyl group is difficult. This problem was dissolved by direct oximation of magnesium phenoxide to salicylaldoxime via hydroxylamine by others.[9]

In order to obtain a pure product, the mid-products should be purified by extracting with solvent and washing with water and by acidic work-up. The yield of reaction in the formylation and oximation steps which are important issue could be also investigated.

The purpose of this research are to characterize and comparing the orthoformylation of Nonylephenol (or phenol) to nonylsalicylaldehyde (or salicylaldehyde) magnesium salt by the direct reaction of solid paraformaldehyde firstly and then its subsequent oximation to nonylsalicylaldoxime. In order to obtain a pure product, the end products should be purified by extracting with solvent and washing with water and by acidic work-up. Characterization and orthoselectivity of this reaction could be studied by instrumental analysis such as ^{1}H-NMR[a], GC/MS[b] and FT-IR[c]. Estimating of reaction yield is also possible by comparing these spectra. In this process the effect of preparation of magnesium phenoxide will be investigated on the orthofromylation of phenol at first. The yields of orthoselectivity of the formylation step could be investigated by the results of reaction on salicylaldehyde and salicylaldoxime products. The yield of oximation processes also could be studied by the interpretation of analyzing results of final product.

Instrumental analysis such as ^{1}H-NMR and FT-IR and GC/MS and interpretation of their spectra could be useful for obtaining the structural information and characterization of mid and end product.

[a]Hydrogen-Nuclear Magnetic Resonance
[b]Gas Chromatography-Mass Spectroscopy
[c]Fourier Transfer Infra Red

MATERIALS AND METHODS

Materials

Phenol (with the melting point of 40-43 ºC and boiling point of 182 ºC) and Hydroxylamine Hydrochloride (with the melting point 156 ºC of and boiling point of 306 ºC) were purchased from Merck chemical company (Germany). Commercial-grades paraformaldehyde (with the boiling point of 120-170 ºC), Nonylphenol (with the melting point of -2 to-8 ºC and the boiling point of 293-297 ºC) and magnesium powder (with the melting point of 650 ºC) were prepared and applied. Experimental-grades toluene and methanol from Mojalleli Chemical Company Tehran-Iran, (with the boiling point of toluene and methanol about of 110.5 ºC, 64.7 ºC respectively) were prepared and applied.

Equipment

A 2 l, round bottom four-necked flask, equipped with mechanical mixture and a condenser, was prepared from Goldis Glassware Company (Tehran, Iran) and applied. An electrical heater was applied for heating.

An FT-IR spectrophotometer, Bomem model MB100, and an NMR spectrometer, (Bruken Drx-500 Avance model, with a 5 mm QNP probe and an internal reference of tetramethyl silane (TMS), were used. GC/MS data were recorded on a Agilent 6890 series GC system and Agilent 5973 network MSD using a 30 m HP-1MS column, 0.25 mm inner diameter, and program temperature 50-275 ºC (15 ºC/min).

Synthesis Technique

At first, magnesium methoxide were prepared from reaction of magnesium powder (12 g, 0.5 mol) in 250 ml. methanol at reflux temperature (64 ºC) in 3 hour. Magnesium bis-nonylphenoxides (or bisphenoxide) were then formed by addition of nonylphenol (224 g, 1mol), (or phenol) to the obtained magnesium methoxide in methane at reflux temperature (64 ºC) for 3 hour too. The methanol solvent was changed by toluene. It was then reacted with paraformaldehyde (83 g, 2.37 mol) in toluene for 5 hour at 90-100 ºC. The excess amount of paraformaldehyde was due to its low reaction rate and for obtaining a high yield. The obtained magnesium nonylphenoxide salt was cooled to 45 ºC and was oximated with a solution of hydroxylmine hydrochloride (69.5 g, 1 mol) in water (300 g) over 1 hour at 45-50 ºC with vigorous stirring. Stirring was continued at 50 ºC for 2 hour. Finally, the magnesium and other impurities were removed by the acidic workup. The end pure product was achieved by acidic and water work

up. Then, the aqueous layers were extracted with toluene or ether too. Afterwards, the all of organic layers were washed with distilled water for the completion of washings. Finally, the obtained organic layer was evaporated under reduce pressure to yield pale yellow liquid pure nonylsalicylaldoxime (and/or salicylaldehyde).

Distillation of methanol should be done slowly so that the concentrations of methanol in the solution should be high at each instance. The result of these processes is that it is an inhibitor in competition with the phenoxide for magnesium coordination. Therefore, this is a controlled reaction, which yields primarily a monoformylated product.

RESULTS AND DISCUSSION

Reaction Scheme of Salicylaldoxime and Salicylaldehyde

The mechanisms of the nonylsalicylaldoxime and salicylaldehyde reactions were shown in the *Figs*. 1 and 2 respectively.

The proposed mechanism of formylation which was presented in *Fig.* 1 for Nonylsalicylaldoxime shows that the formed magnesium ligand how protects oxygen atoms of the phenolic hydroxyl group and causes the orthoselectivity of formylation. Magnesium bisphenoxides containing two phenoxide residues per magnesium atom is more stable due to the electro-donating effects of aryl residue in this compound. The magnesium atom of the formed magnesium bisphenoxide salt coordinate with the oxygen atoms of both phenoxide and methoxide neighboring thus is less available for coordinating with formaldehyde oxygen. Formaldehyde is naturally in the gaseous form which is less available but paraformaldehyde is solid and has polymer formula with a few formaldehyde chains. Paraformaldehyde releases formaldehyde atoms during reaction. Magnesium salt in methanol is not efficiently formylated by formaldehyde. Substitution of methanol by toluene by distillation, followed by the addition of paraformaldehyde at around 95 ºC (with removal of volatile reaction by-products by distillation) gives the corresponding salicylaldehyde magnesium salts as a result of formylation at the position *ortho* to the parent phenol hydroxyl. Oximation of the obtained salicylaldehyde magnesium salts is facilitated without the removing of magnesium. *Fig*. 2 shows the orthorformylation of the phenol.This process is much difficult than the nonylphenol, due to having *metha* free position.

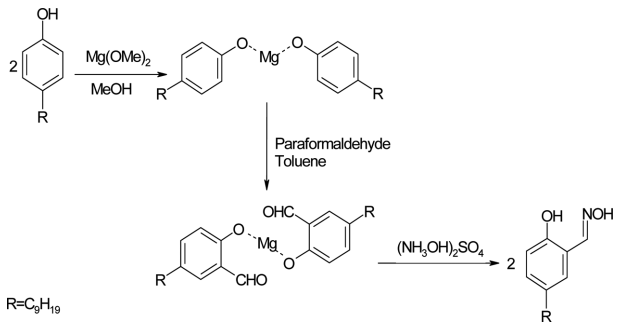

***Fig*. 1.** The reactions of salicylaldehyde production.

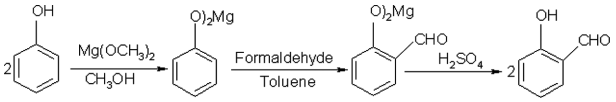

***Fig*. 2.** Proposed mechanism of Nonylsalicylaldoxime production.

The ^{1}H-NMR, FT-IR, and GC/MS spectra of nonylsalicylaldoxime and salicylaldehyde were taken and they would be interpreted in the next sections.

^{1}H-NMR Spectra

The ^{1}H-NMR spectrum of nonylsalicylaldoxime was taken. The peaks of nonyl protons were shown at δ 0.8-1.7. The sharp peak of methyl protons of toluene appeared at 2.4 ppm. The multiple peaks around δ 6.9-7.33 could be assigned to the aromatic protons. The sharp peak of CH=N was observed at δ 8.3, that is to say, the oxime bond in final product has been formed. The sharp singlet of the oxime hydroxyl group was seen at δ 9.95. This peak shows the development of oximation reaction. The aldehyde which must be shown as the unoximated aldehyde had the signals of phenolic hydroxyl protons appeared at δ 10.8 and δ 11. These peaks show that the unoximated has been removed and the oximation reaction hasn't been completed. But the difference of their integrated value (0.153 versus 1.000) is very low i.e. the conversion of oximation is about 85%.

Moreover there are other ways to investigate the conversion value of formylation and oximation reactions in the production of nonylsalicylaldoxime using the ^{1}H-NMR spectrum. The comparison of aldehyde or hydroxyl of oxime group versus unreacted hydroxyl group of phenolic protons could show the yield of formylation reaction. The hydroxyl group of phenolic which should be appeared at about 11 ppm and the aldehyde peak which should be appeared at about 10 ppm are very low. The hydroxyl peaks of oxime reaction is appropriately good and these show the high yield of formylation reaction (about 90%). ^{1}H-NMR comparison against a reference standard confirms the formation of desirable product.[19,20]

The ^{1}H-NMR (500 MHz) spectrum of salicylaldehyde was taken. The multiple peaks appeared at the chemical shifts of 7-7.6 ppm could be assigned to aromatic protons. The sharp peak appeared at 9.9 ppm is due to the resonance of aldehyde proton. The sharp peak that has shown at the chemical shift 11.07 ppm could be assigned to the proton of phenolic hydroxyl group.

Comparison of these two peaks show that the multiple peaks at δ 0.8-1.7 which is assigned to nonyl did not appeared at the salicylaldehyde ^{1}H-NMR spectrum. The peak appeared at 2.4 which is due to the trace amount of toluene solvent has been appeared too. The peak of CH=N was observed at δ 8.3, the oxime peaks in final product, have not been formed in the salicylaldehyde not at all.

The phenolic proton of unreacted phenol was appeared at 4.02 ppm but their integration values in both ^{1}H-NMR figures of salicylaldehyde and nonylsalicylaldoxime are too small to be accounted. This means that conversion of phenol to magnesium phenoxide was accurately completed. The integration value of aldehyde protons is about 0.94 and for the phenolic one in orthoformylated product is about 0.92. These similarities imply on the high conversion of reaction. As a result it could be concluded that the conversion of reaction is very high. As about selectivity since there is any multiple peaks at phenolic or aldehyde proton position (i.e. *meta* and *para*). It could be deduced that the production of other formylated sequences is so few to be considered.[19,20]

GC/MS Spectra

GC/MS chromatogram was used for detection of Nonylsalicylaldoxime by Mw=263 and has been shown in the *Fig*. 3. The peak at 26.48 min and having m/z 281.1 could be assigned to the Nonylsalicylaldoxime. This spectrum emphasize on the formation of final product, reasonably. The appearance of other peaks is due to the using of the industrial grades of materials nonylphenol or the trace reminds raw materials. i.e., the peaks appeared below 16 minute should be for the trace of toluene which has been used as solvent.

The GC-MS chromatogram of product as shown in *Fig*. 4 was used for detection of salicylaldehyde in the obtained product. The GC-MS chromatogram consists of a main peak at 6.48 min, which is due to the 2-hydroxybenzaldehyde product. In addition, the peak appeared at retention time 5.59 min could be due to presence of unreacted phenol in product, but as seen by GC-MS its extent is too little. The major by-product from the reaction could be the 2,2′-dihydroxydiphenilmethane which was identified at retention time 14.77 min and its area% is 10.72. The amount of byproducts -calculated from the area of their peaks which given from quantitative chromatographic analysis is up to 20%. The extent of detected *p*-hydroxybenzaldehyde at 8.97 min is less than 0.6% (w/w). Therefore, approximately 80% of product is salicylaldehyde. This can be confirmed the result of ^{1}H-NMR spectrum. The high-yield of synthesized salicylaldehyde, indeed confirms the method that described in this paper.

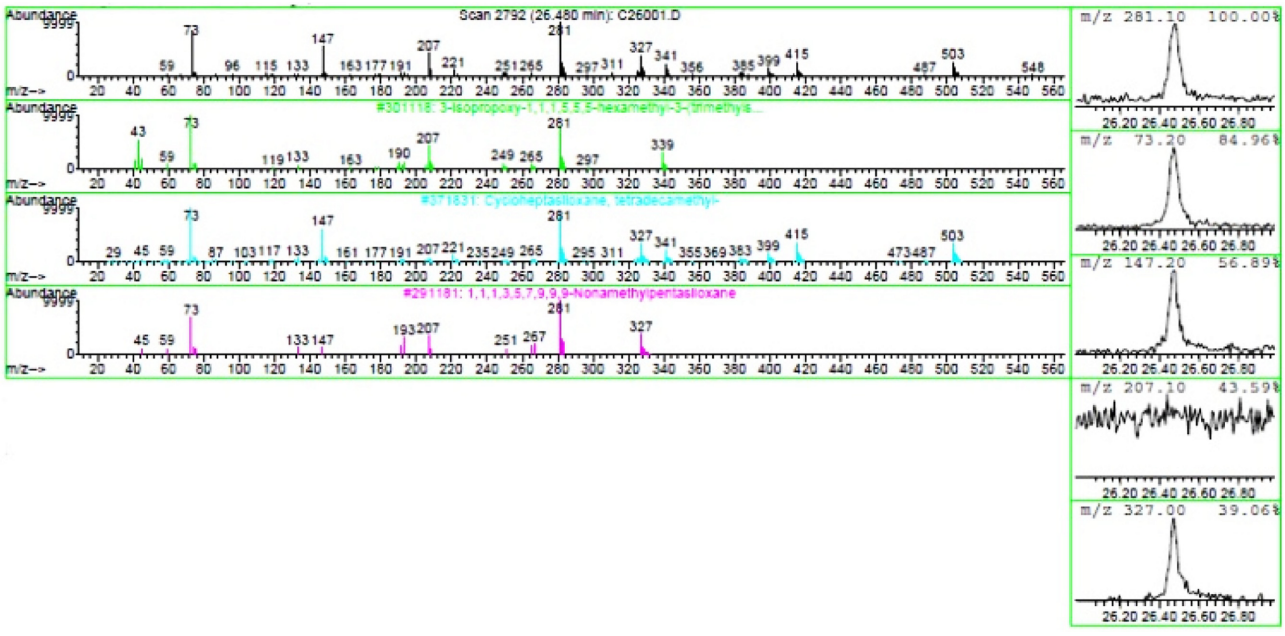

***Fig*. 3.** GC-MS chromatogram of the 5-nonylsalicylaldoxime.

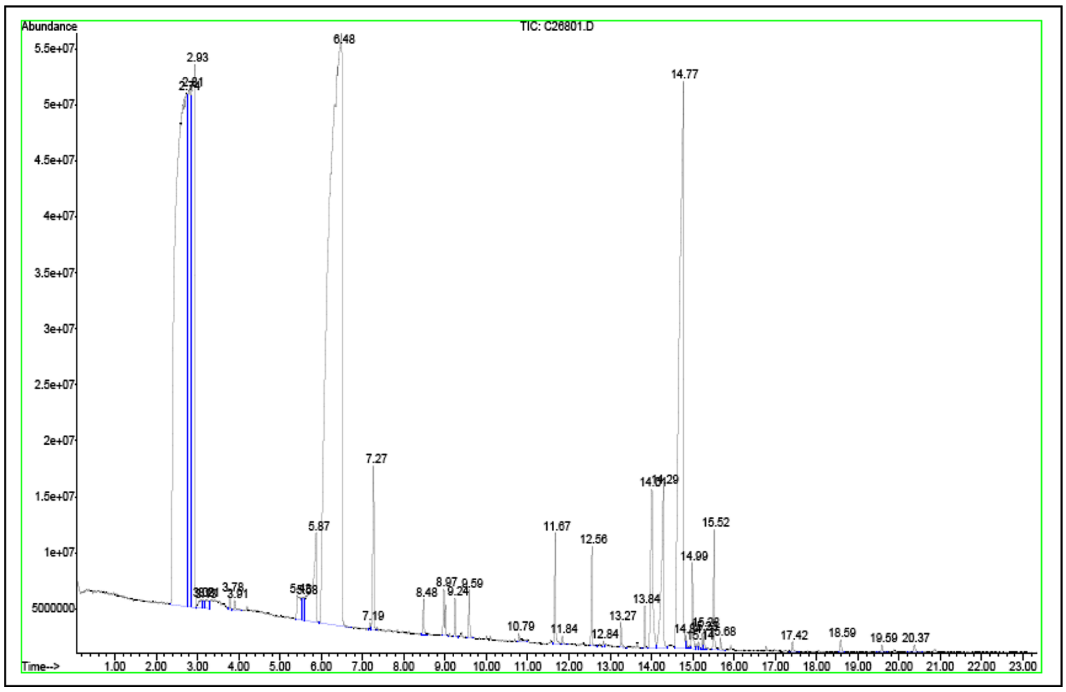

***Fig.* 4.** GC-MS chromatogram of the salicylaldehyde.

The FT-IR Spectrum

The FT-IR Spectrum for the oxime compound of Nonylsalicylaldoxime shows an OH stretching vibration in the 2900-3500 cm^{-1} region which should be due to phenolic and oxime hydroxyl and also due to the C-H band in nonyl and oxime. The band at 1623 cm^{-1} should be due to C=N Oxime. The vibration band appeared at 1585 cm^{-1} could be assigned to the C=C band in aromatic ring.[21]

The FT-IR spectra of final salicylaldehyde was recorded too. The appeared peak at 2847cm^{-1} should be due to the C-H band of aldehyde group while in the previous spectra it was very small. Carbonyl group should have a lower stretching frequency due to the presence of phenolic hydroxyl group. Hence, the broad band appeared at 1664 cm^{-1} should be due to aldehyde carbonyl group. Therefore, by comparing the obtained spectroscopic data with the literature data it is qualitatively evident that salicylaldehyde was produced with a high conversion and selectivity. At a result, it is evident that formylation validates from this figure and oximation is obvious from the spectrum of previous figure.

CONCLUSION

It is evident that nonylphenol (or phenol) could not be formylated without protecting its hydroxyl group. In this research it was recognized that magnesium nonylphenoxide (or phenoxide) could be orthoformylated using paraformaldehyde by a high yield and high selectivity. It was found that if the formylation reaction carry out at suitable conditions of time and temperature and the methanol solvent collects on time slowly it will result a high yield and high selective product. Comparison of Salicylaldoxime and Salicylaldehyde spectra (mainly H-NMR) showed that methoxylation reaction was almost completed. Formylation reaction in both compounds has had a conversion about 90% and the conversion of oximation reaction was about 85%. Although the yield of formylation and oximation reaction was appropriately good but it is suggested that the extra amount of paraformaldehyde and hydroxylamine be applied and also giving more time to the reaction may have a significant effect on their conversion. Moreover using a phase transfer catalyst also might increase the reaction conversion especially for salicylaldehyde.

REFERENCES

1. Kordosky, G. A. *Solvent Extraction Reagents and Applications*; MCT Redbook, Cognis Corporation Publisher: U.S.A., 2007.
2. Smith, A. G.; Tasker, P. A.; White, D. J. *Coord. Chem.*

Rev. **2003**, *241*, 61.
3. Habbache, N.; Alane, N.; Djerad S.; Tifouti, L. *Chem. Eng. J.* **2009**, *152*, 503.
4. Forgan, R. S. Ph.D. Thesis, University of Edinburgh, 2008.
5. Ritcey, G. M.; Singhua, T. *Sci. Tech*. **2006**, *11*, 137.
6. Kirk, R. E.; Othmer, D. F. *Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1991; pp 1030-1042.
7. Vogel, A. I. *A Text Book of Organic Chemistry*; Addison-Wesley Pub. Co.: 1991.
8. Thoer, A.; Denis, G.; Delmas, M.; Gaset, A. U.S. Pat. 4755613, 1988.
9. Aldred, R.; Johnston, R.; Levin, D.; Neilan, J. *J. Chem. Soc., Perkin Trans*. **1994**, *1*, 1823.
10. Levin, D. U.S. Pat. 5502254, 1996.
11. Dimmite, J. H.; Kearns, M. A.; Chambless, W. H. U.S. Pat. 6288276, 2001.
12. Matsuda, T.; Murata, T. U.S. Pat. 4231967, 1980.
13. Beswick, G. E. U.S. Pat. 4085146, 1978.
14. Paliwal, S. B.; Mathur, V. B.; Mirani, B. N. WO 2007/034501, 2007.
15. Lindoy, L. F.; Meehan, G. V.; Svenstrup, N. *Synthesis* **1998**, 1029.
16. Casiraghi, G.; Casnati, G.; Cornia, M.; Pochini, A.; Puglia, G.; Sartori, G.; Ungaro, R. *J. Chem. Soc. Perkin Trans*. **1978**, *1*, 318.
17. Willemse, J. A., MSc. Thesis, University of Rand Afrikaans, 2003.
18. Hofsløkken, N. U.; Skattebøll, L. *Acta Chemica Scandinavica* **1999**, 258.
19. Kasler, F. *Quantitative Analysis by NMR Spectroscopy*; Academic Press Inc.: London and New York, 1973; p 130.
20. Silverstein, R. M.; Bassler G. C.; T. C., Morill *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1991.
21. Mohan, J. *Organic Spectroscopy: Principles and Applications*; Narosa Publishing House: India, 2000.