



Steric effects on o-(N,N-disubstitutedamino)-thiophenols [pt. I] Synthesis of
1,1-dimethyl-2,3-dimethylenecyclopropane from delta-3-carene [pt. II]
by Steven Wayne Miller

A thesis submitted to the Graduate Faculty in partial fulfillment of the Requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

The product obtained from the alkaline hydrolysis of the quaternary salt, 2-methyl-3-ethylbenzothiazolium iodide, was determined to have the structure shown below. This product, o-(N-ethyl-N-acetylamino)-thiophenol, gave rise to a complex nmr spectrum. The methylene protons of the ethyl group appeared to be nonequivalent giving rise to two sets of equal multiplets. If the methylene protons were equivalent, then they should give a quartet. Because of this nonequivalence, several related compounds, with differing steric interactions, were prepared and from these compounds the steric requirements for restricted rotation around the aryl to nitrogen bond were determined.

The nmr spectrum, uv spectrum and the mass spectrum of the product of the pyrolysis of 1,1-dimethyl-2,3-bis-(dimethylamino-methyl)-cyclopropane dimethoxide indicated that 1,1-dimethyl-2,3-dimethylenecyclopropane had been prepared. The dimethoxide was synthesized from delta-3-carene. Catalytic hydrogenation of the dimethylene offered further proof for the proposed structure of the diene. The spectral data on the hydrogenated product indicated that it was 1,1,2,3-tetramethylcyclopropane.

(Formula not captured by OCR) (Formula not captured by OCR)

I. STERIC EFFECTS IN α -(N,N-DISUBSTITUTEDAMINO)-THIOPHENOLS
II. SYNTHESIS OF 1,1-DIMETHYL-2,3-DIMETHYLENECYCLOPROPANE FROM
DELTA-3-CARENE

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Approved:


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To
Dad

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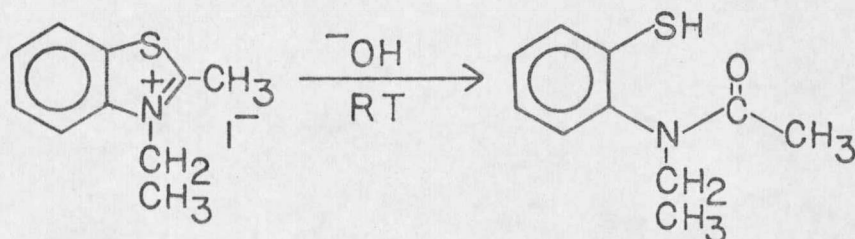
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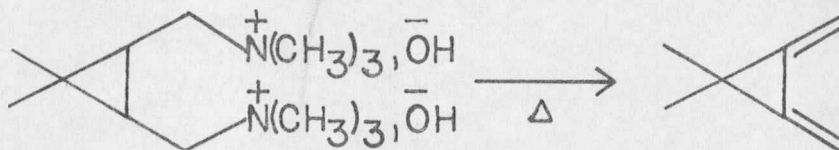
ABSTRACT

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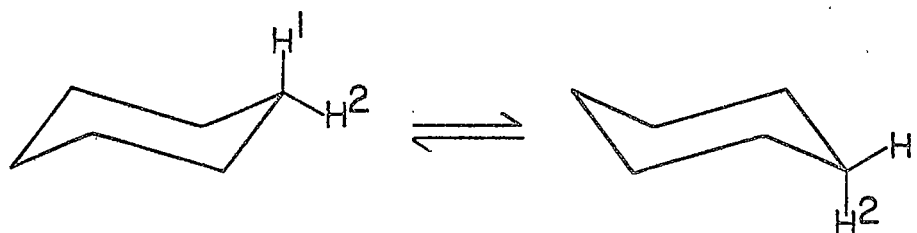
PART I

STERIC EFFECTS IN o-(N,N-DISUBSTITUTEDAMINO)-THIOPHENOLS

INTRODUCTION

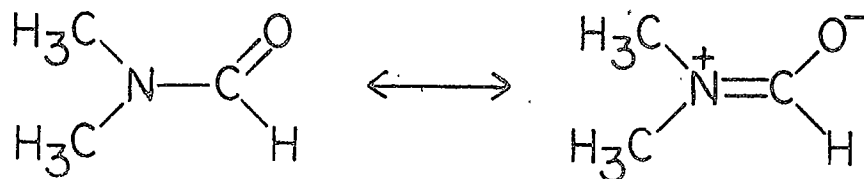
During the investigation of the hydrolysis of certain cyanine dyes and quaternary salts it was noted that certain of the products had unusual nmr spectra. A further and systematic investigation into the origins of these unusual spectra is the focus of this portion of the thesis. Because nuclear magnetic resonance spectroscopy is such a powerful tool to the organic chemist and because it plays a central role in the remainder of this thesis it is appropriate to summarize the salient features of the method which apply to this discussion.

Nuclear magnetic resonance spectroscopy has developed into a powerful tool for the organic chemist. Not only is nmr spectroscopy one of the chemist's most valuable tools for probing the structure and stereochemistry of complex molecules, but it also provides him with a means of studying intramolecular movements with activation energies of 5 to 25 kcal./mole. ⁽¹⁾ For example, it is well known that equatorial and axial protons of cyclohexane have considerably different chemical shifts. ⁽²⁾ However, at room temperature, all the protons of cyclohexane appear as a single narrow peak, due to the inversion of the ring. When the temperature is sufficiently lowered, so that the inversion can be seen on the nmr



time scale, separate peaks are seen for the axial and the equatorial protons. (3) In other words, at normal temperatures, the inversion or flipping of the cyclohexane ring is fast, according to the nmr time scale, and what is observed is an average of the protons.

Nuclear magnetic resonance spectroscopy is also of great importance to the organic chemist in the detection of hindered rotation about a bond in a molecule. (4) The rotation around a bond in a molecule can be affected by electronic and steric factors. The most obvious electronic factor would be that of a double bond in an alkene. A more subtle electronic factor would be partial double bond character as in an amide. The foregoing is readily seen in the nmr spectrum of dimethylformamide or dimethylacetamide



in which the gem dimethyl groups in either case are not equivalent.⁽⁵⁾ The second reason affecting rotation about a bond, that of steric hindrance, can be seen in the well-known examples of the biphenyl derivatives.^(4,6) This steric hindrance has also been observed in the rotation about the aryl to carbonyl bond in substituted benzamides^(4,7-11) and benzophenones⁽⁴⁾, and also in the aryl to nitrogen bond in anilines^(4,12), nitrosoanilines^(12,13), N-aryl pyrroles⁽¹⁴⁾ and anilides.^(4,15-25) This latter example, that of steric hindrance in the rotation around the aryl to nitrogen bond in N,N-disubstituted o-aminothiophenols (N-substituted acetanilides), will be the main concern of Part I of this thesis.

However, this study of sterically hindered rotation in anilides was not an original aim of the research, but it arose from the results obtained during the course of work on the original project. Initially, the research project involved the hydrolytic and photolytic decomposition of representative cyanine dyes. This project was of interest, as the cyanine dyes are employed in many photographic and bio-medical applications^(12,13), but there was no information available as to their mode of decomposition in solution, on surfaces or in living systems. Since there is considerable interest and investigation of the cyanines in the bio-medical field, it would be of importance to gain knowledge of their hydrolytic reactions to aid in interpreting and understanding possible modes of action.

