

MANNICH CONDENSATIONS OF 2-NAPHTHALENETHIOL

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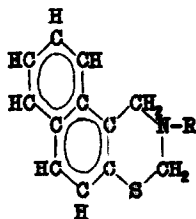
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Only one reference appears in literature for the Mannich Condensation of thiophenols. Grillo¹ reported the condensation of the secondary amines, morpholine, piperidine, and diethylamine, with formaldehyde and various thiophenols.

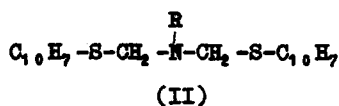
Although there are several references to the Mannich Condensation of phenols, formaldehyde, and primary amines, there are no reported Mannich Reactions involving thiophenols and primary amines.

In this investigation, 2-naphthalenethiol was condensed with formaldehyde and various primary amines in a 1:2:1 mole ratio, respectively, with view of securing 2-alkyl-2,3-dihydro-1H-naphth[1,2-e]/[1,3]thioxazines (I). In lieu of the desired thioxazines (I), a new series of compounds, the bis(2-thionaphthoxymethyl)-alkyl-amines (II) were isolated in good yields. Elementary carbon, hydrogen, and nitrogen analysis check for the theoretical values for compounds II obtained from tertiary-butylamine, tertiary-octylamine, isopropylamine, cyclohexylamine, methylamine, and benzyl amine. The analysis were performed by Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck-Institut für

Kohlenforschung, Ruhr, Germany.



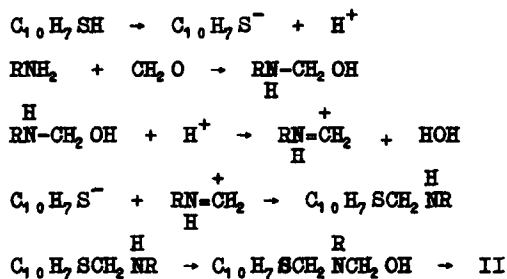
(I)



In case of benzylamine, benzylaminomethyl-(2-naphthyl)-sulfide (III) was also isolated. The absence of an infra-red band in the area of 3.9 microns for all products indicated that the Mannich bases, 1-alkylaminomethyl-2-thionaphthol (IV) were not secured.

Compound III appeared to be stable in alcoholic solutions, even upon warming. This is in contrast to the instability reported² for 1-benzylaminomethyl-2-naphthol, which decomposes in alcoholic solutions at temperatures as low as 5° to N,N-bis(2-hydroxy-1-naphthylmethyl)-benzylamine. However, morpholinoaminomethyl-(2-naphthyl)-sulfide (V) could not be isolated when the reactants were condensed in alcoholic solutions; 2-naphthyldisulfide, $(\text{C}_{10}\text{H}_7)_2\text{S}_2$, was secured. Similar results were obtained when dioxane was used as the solvent. In lieu of the solvents (methanol, ethanol, dioxane) normally used in our laboratories for Mannich-Reactions, it was found convenient to use ethyl acetate for all condensations in this investigation.

The fact that the hydrogen of the -SH group of the 2-naphthalenethiol is displaced rather than the alpha-hydrogen as in 2-naphthol², is probably due to the relatively high acidity of 2-naphthalenethiol. The following mechanism is suggested for the condensation:



ACKNOWLEDGEMENTS

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REFERENCES

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- (2) W.J. Burke, W.A. Nasutavicus, C. Weatherbee, J. Org. Chem. 29, 407 (1964)